

General Disclaimer

One or more of the Following Statements may affect this Document

- This document has been reproduced from the best copy furnished by the organizational source. It is being released in the interest of making available as much information as possible.
- This document may contain data, which exceeds the sheet parameters. It was furnished in this condition by the organizational source and is the best copy available.
- This document may contain tone-on-tone or color graphs, charts and/or pictures, which have been reproduced in black and white.
- This document is paginated as submitted by the original source.
- Portions of this document are not fully legible due to the historical nature of some of the material. However, it is the best reproduction available from the original submission.



UNCLASSIFIED

SEPARATOR DEVELOPMENT FOR A HEAT STERILIZABLE BATTERY

L. C. Scala, A. Langer, G. D. Dixon
R. G. Charles, C. R. Ruffing, L. A. Doggrell

April 24, 1969



Contract No. 951525

"This work was performed for the Jet Propulsion Laboratory, California Institute of Technology, pursuant to a sub-contract issued under Prime Contract NAS 7-100 between the California Institute of Technology and the United States of America represented by the National Aeronautics and Space Administration."

Westinghouse Electric Corporation
Research Laboratories
Pittsburgh, Pennsylvania 15235

Final Report

Period: June 1, 1966 to December 31, 1968

FACILITY FORM 802	<u>NA-33801</u>	_____
	(ACCESSION NUMBER)	(THRU)
	<u>126</u>	<u>1</u>
	(PAGES)	(CODE)
<u>CR-103888</u>	<u>03</u>	_____
(NASA CR OR TRX OR AD NUMBER)	(CATEGORY)	

NOTICE

This report was prepared as an account of Government-sponsored work. Neither the United States, nor the National Aeronautics and Space Administration (NASA), nor any person acting on behalf of NASA:

- a. Makes warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately-owned rights; or
- b. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used above, "person acting on behalf of NASA" includes any employee or contractor of NASA, or employee of such contractor, to the extent that such employees or contractor of NASA, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment with such contractor.

Requests for copies of this report should be referred to:

National Aeronautics and Space Administration
Office of Scientific and Technical Information
Washington 25, D. C.

Attention: AFSS-A

UNCLASSIFIED

SEPARATOR DEVELOPMENT FOR A HEAT STERILIZABLE BATTERY

L. C. Scala, A. Langer, G. D. Dixon
R. G. Charles, C. R. Ruffing, L. A. Doggrell

April 14, 1969

Contract No. 951525

"This work was performed for the Jet Propulsion Laboratory, California Institute of Technology, pursuant to a sub-contract issued under Prime Contract NAS 7-100 between the California Institute of Technology and the United States of America represented by the National Aeronautics and Space Administration."

Westinghouse Electric Corporation
Research Laboratories
Pittsburgh, Pennsylvania 15235

Final Report

Period: June 1, 1966 to December 31, 1968

TABLE OF CONTENTS

	<u>Page</u>
1. INTRODUCTION	1
2. OBJECTIVES	1
3. EXPERIMENTAL AND RESULTS	3
3.1 FIRST PHASE	3
3.1.1 <u>Test Equipment</u>	3
3.1.1.1 Electric resistance of battery separator by a d.c. method	3
3.1.1.2 Resistivity measurements by an a.c. method	4
3.1.1.3 A polarographic device for measuring the diffusion of zincate ion through battery separators	4
3.1.1.4 Electrolyte diffusion through separator membranes	5
3.1.2 <u>Organic Substrates</u>	5
3.1.3 <u>Inorganic Filler Materials</u>	5
3.1.4 <u>Polymeric Binders</u>	6
3.1.5 <u>Membrane Fabrication</u>	7
3.1.5.1 Evaporation of solvent by heat	8
3.1.5.2 Extraction of solvent by water or by acetic acid	9
3.1.6 <u>Membrane Properties</u>	9
3.1.6.1 Effect of solvent on thickness and resistivity	9
3.1.6.2 Effect of filler properties and treatment on thickness and resistivity	12
3.1.6.2.1 Effect of ball milling of filler suspensions.	13
3.1.6.3 Effect of pressure on experimental separators	14
3.1.6.3.1 Methods of pressure application	14

TABLE OF CONTENTS (cont.)

	<u>Page</u>
3.1.6.3.2 Effects of pressure on resistivity of films	15
3.1.6.3.3 Effects of pressure on films with varied amounts of filler	15
3.1.6.4 Behavior of membranes on sterilization testing	16
3.1.6.5 Zn dendrite penetration through separators . .	17
3.1.6.6 Silver ion diffusion	21
3.1.6.7 Tensile strength of films	23
3.1.7 <u>Chelate Modifications</u>	23
3.1.8 <u>Conclusions from First Phase</u>	26
3.2 SECOND PHASE	26
3.2.1 <u>Test Equipment</u>	28
3.2.2 <u>Organic Substrates</u>	28
3.2.3 <u>Inorganic Fillers</u>	31
3.2.4 <u>Polymeric Binders</u>	31
3.2.5 <u>Wetting Agents</u>	32
3.2.6 <u>Apparatus and Procedures</u>	32
3.2.6.1 Hand-coating devices	32
3.2.6.2 Laboratory-size continuous coating apparatus	33
3.2.6.3 Methods for application of coating mixture to supporting tape	34
3.2.6.4 Continuous dip-coating in industrial coating tower	35
3.2.7 <u>Formulations</u>	37
3.2.8 <u>Membrane Properties</u>	37
3.2.8.1 Effects of extraction time	37
3.2.8.2 Effects of variations of oxide loadings . . .	39

TABLE OF CONTENTS (cont.)

	<u>Page</u>
3.2.8.3 Effect on resistance of time of soaking in KOH	40
3.2.8.4 Sterilization tests	40
3.2.8.5 Effects of oxide loadings and concentra- tion of wetting agents on sterilization results	42
3.2.8.6 Determination of silver ion diffusion through membranes	43
3.2.8.7 Determination of zinc ion diffusion rates . .	45
3.2.8.8 Effect of aging in 40% KOH with silver present	45
3.2.8.9 Effect of addition of free zirconia to sterilization system	46
3.2.8.10 Pressure on continuously fabricated separators	47
3.2.9 <u>Preparation of Foot Wide Sterilizable Separator</u> <u>Material</u>	47
4. CONCLUSIONS AND RECOMMENDATIONS	52

LIST OF TABLES

- Table I - Sterilization of Polymeric Candidates
- Table II - Solubility of Inorganic Filler Materials in 40% KOH
- Table III - Battery Separator Compositions
- Table IV - Electrical Characteristics of Experimental Membranes
- Table V - Effects of Extraction by Water-DMAC Solutions
- Table VI - Weight Change of Water-Precipitated Membranes on Sterilization Cycling
- Table VII - Filler Residue After Sterilization Cycling
- Table VIII - Effect of Excess Filler on Filler Residue after Sterilization
- Table IX - Membrane Tensile Strength
- Table X - 8-Hydroxyquinoline Derivatives of Structure I
- Table XI - Epoxy Resins Containing 8-Hydroxyquinoline Groupings
- Table XII - Interaction of Modified Epoxy Resins with Copper Acetate or NaOH
- Table XIII - Resistivity of PS Films Containing Chelating Epoxies as Fillers
- Table XIV - Identification of Samples for Sterilization Tests
- Table XV - Effect of Sterilization Cycling on Thickness, Resistivity and Weight
- Table XVI - Effect of Oxide and Wetting Agent Concentrations on Thickness, Resistivity and Weight after Sterilization Cycling
- Table XVII - Effect of Excess Zirconia (10%) on Sterilized Membranes
- Table XVIII - Effect of Excess Zirconia (30%) on Sterilized Membranes
- Table XIX - Sterilization Results on 3 and 12 Inch Wide Composites
- Table XX - Sterilization Results on 12 Inch Wide Pellon 2140- and Webril EM 476- Containing Composites

LIST OF ILLUSTRATIONS

- Fig. 1 - Resistivity Tester - D.C. Method
- Fig. 2 - Diffusion Testing Apparatus with Polarographic Sensing
- Fig. 3 - Continuous Coating Machine
- Fig. 4 - Filler Distribution in Membranes
- Fig. 5 - Cross Section of Polysulfone Without Filler
- Fig. 6 - Resistance vs. Film Thickness
- Fig. 7 - Blade Setting vs. Dry Film Thickness
- Fig. 8 - Resistance vs. Film Thickness, Zeolon H
- Fig. 9 - Resistance vs. Film Thickness, TiO_2
- Fig. 10 - Resistance vs. Film Thickness, ZrO_2
- Fig. 11 - Cross Section of Polysulfone with 25% ZrO_2
- Fig. 12 - Resistance vs. Film Thickness, Zeolon H on Webril
- Fig. 13 - Relation Between Ball-Milling Time and Resistance
- Fig. 14 - Relation Between Compression Pressure and Resistivity, Low Oxide Loading
- Fig. 15 - Relation Between Compression Pressure and Resistivity, High Oxide Loading
- Fig. 16 - Influence of Amount of Filler on Resistance
- Fig. 17 - Dendrite Penetration Tester
- Fig. 18 - Dendrite Penetration Time - Current Density Relations
- Fig. 19 - Polarograms of Different Silver Concentrations
- Fig. 20 - Relation Between i_d and Silver Concentration
- Fig. 21 - Relation Between Silver Concentration i_d and Diffusion Time
- Fig. 22 - Laboratory Size Continuous Coating Machine
- Fig. 23 - Industrial Tower Setup for Continuous Coating
- Fig. 24 - Electrolyte Diffusion Time - Bare Webril

LIST OF ILLUSTRATIONS (cont.)

- Fig. 25 - Electrolyte Diffusion Time - FUDO Cellophane
- Fig. 26 - Electrolyte Diffusion Time - Composite
- Fig. 27 - Effect of Exposure to KOH on Resistance
- Fig. 28 - Electrolyte Diffusion Time Through Pellon Composite

SEPARATOR DEVELOPMENT FOR A HEAT STERILIZABLE BATTERY

L. C. Scala, A. Langer, G. D. Dixon
R. G. Charles, C. R. Ruffing, L. A. Doggrell

ABSTRACT

Battery separator materials capable of withstanding a sterilizing cycle of 60 hours in 40% KOH at 135°C have been fabricated using a continuous dip-coating process.

The final separator coating formulation chosen for best results consists of a 3:1 mixture by weight of previously dried and ball-milled 20:50 mesh Bio-Rad hydrated zirconia filler, with Union Carbide PS 1700 polysulfone in dimethylacetamide (DMAC), in the presence of 1% by solid weight of a wetting agent. This mixture is coated on to non-woven, KOH-resistant polypropylene tape (Webril EM 476, 0.0027 inch thick, or Pellon 2140, 0.007 inch thick) by a continuous dip-coating process. The resulting composite is passed through a dioxane:water bath, where the solvent DMAC still present is leached out and the polysulfone is precipitated as a continuous solid film on the tape. This action results in the formation of extremely small pores throughout the composite through which passes the electrolyte. The residual water and solvent are removed from the continuous separator composite by heating at 75-80°C in a 12 foot long vertical tower. Acceptable coating speeds range from 4 to 8 feet per minute, the preferred speed being 7 ft./min.

Separator materials obtained as outlined above exhibited specific resistivities before sterilization of the order of 20-50 ohm-inch in the case of Webril-supported composites. Specific resistivity values of Pellon-supported composites were of the order of 100-150 ohm-inch, well above the tolerable maximum of 59 ohm-inch. However, prolonged exposure to a high temperature sterilizing cycle in concentrated alkali reduced the resistivity values of the Pellon tapes to below the tolerated maximum. The same effect was observed in the Webril-supported composites.

Silver ion flow through these separators was very low, in the worst case being less than 4 ppm in about 50 hours' exposure to a saturated KOH-Ag solution. Zincate ion diffusion was also very low, with a maximum passage of 4.2 ppm after 150 hours. Long term aging of these sterilizable membranes in KOH with silver present had generally little deleterious effects on the specific resistivity of these samples. The electrolyte flow through Webril-supported membranes was faster than that through FUDO films by a factor of about 4. The Pellon-supported composites hindered the electrolyte flow to some extent; however, on continuous exposure to 40% KOH the flow increased to an acceptable level.

Webril-supported and Pellon-supported separator membranes remained dimensionally stable and retained their useful properties after one sterilizing cycle consisting of exposure to 40% KOH for 65 hours at 135°C. The generally very small weight losses occurring on sterilization cycling were reduced by adding free zirconia to the sterilizing cells in the amount of 10-30% by weight of the separator composite.

Epoxy resins were modified with chelating 8-hydroxy quinoline derivatives to provide structures expected to inhibit the free passage of silver and zinc ions while allowing the transport of hydroxyl ions and water molecules. Separators made using these resins in place of the inorganic filler exhibited no appreciable advantage over separators containing zirconia.

Several dozen feet of one foot wide separator material fabricated continuously using a modified industrial coating tower were delivered to JPL for testing.

1. INTRODUCTION

This report covers the work performed for the Jet Propulsion Laboratory, California Institute of Technology, sponsored by the National Aeronautics and Space Administration under Prime Contract-NAS 7-100, Contract No. 951525, over the period June 1, 1966 to October 31, 1968.

The work described in this report is divided into two phases: the first phase was headed by Dr. A. Langer and concerned itself primarily with screening and preliminary testing of battery separator materials; the second phase, managed by Dr. L. C. Scala, involved further screening, the establishment of procedures for producing separator material continuously, and the supply of one foot wide separator tape to J.P.L.

2. OBJECTIVES

It is postulated that a proper separator in a heat sterilizable silver-zinc secondary battery should perform several functions satisfactorily after being subjected to heat sterilization treatment. Among these are the following:

1. It must prevent direct contact between the positive and negative electrodes to avoid internal discharge. The separator must therefore remain a good electronic insulator.
2. It should allow a high degree of ionic conduction when soaked with the electrolyte to minimize the internal IR drop of the battery at high discharge and charge rates and to assure high efficiency in utilization of the active components.
3. It should retard to some degree the free diffusion of some of the soluble complexes formed, notably of Ag, to prevent migration to and deposition on the Zn electrode. A certain amount of Zn diffusion must be maintained to assure capacity of the cell.
4. The separator should retard the dendritic growth of the Zn in the charging cycle, so that the zinc dendrites cannot reach the opposite electrode, causing internal shorts and loss of active material.

The separator material must be stable against the degrading influence of higher silver oxides during and after exposure to several heat cycles at 135°C for 60 hr. duration while in contact with the 40% KOH electrolyte, so that it will still perform the above functions. Among its other required properties, the barrier should have and maintain satisfactory mechanical strength to prevent tearing; it should also be flexible and free from imperfections, such as pinholes and cracks. The total thickness, which should not exceed 6 mils, should preferably be achieved by the use of multiple wraps of thinner membranes.

Composite separators, prepared by a variety of fabrication procedures, were to be characterized by several types of property measurement, including:

1. Electrical conductivity measurements.
2. Determination of selective permeability for zinc and silver complexes.
3. Measurement of alkali diffusion rate.
4. Microscopic and electrographic inspection for pinholes and cracks.
5. Shear and tensile strength and thickness measurements.
6. Evaluation of resistance to dendritic penetration.
7. Determination of other properties as necessary.

Some of these measurements were made only on selected membranes.

The first phase of this project was an exploratory study of composite separators that may possibly perform the above functions and possess the desired properties. We intended to modify organic matrix materials which have the satisfactory stability in the given environment by incorporation of ion permeable inorganic materials stable under the same conditions. It was believed that inorganic ion exchange substances (natural and artificial zeolites) or substances with many molecules of

water of hydration, forming inorganic gels, may best meet this purpose. A secondary effort was devoted to modification of macroporous and microporous organic matrices by attachment of chelating functional groups.

The second phase of this project had as a final aim the establishing of methods for the continuous production of one foot wide battery separator material. This also involved further testing of separator material ingredients.

3. EXPERIMENTAL AND RESULTS

3.1 FIRST PHASE

3.1.1 Test Equipment

3.1.1.1 Electrical resistance of battery separators by a direct current method

Because of the importance of separator resistance to the successful functioning of a battery, two methods were used to measure this property. The instrument for resistivity measurements by the direct current method was patterned closely after that described by Lander.* Only minor changes in design were made for ease of operation. A photograph of the cell is shown as Figure 1.

A closed system is employed for filling and emptying the cell without exposing the concentrated KOH solution to air.

The cadmium electrodes were of the sintered type found in commercial nickel-cadmium batteries. They were partially charged before use by substituting a nickel foil for the membrane and applying a potential between the nickel and the two cadmium electrodes.

For a measurement of membrane resistivity, a potential is applied between the two cadmium electrodes, sustaining a current of 20 ma.

* J. J. Lander in "Characteristics of Separators for Alkaline Silver Oxide Zinc Secondary Batteries - Screening Methods", J. E. Cooper and A. Fleischer, Editors, A. F. Aero Propulsion Laboratory (1965), Chapter 6a, p. 53.

The resistance is calculated from the potential difference between the two reference electrodes. The maximum specific resistivity allowed by the contract was 150 ohm-cm (or 59 ohm-inch).

3.1.1.2 Resistivity measurements by the ac method

The second apparatus built for membrane resistivity measurements uses an alternating current bridge method. The instrument is similar to a recent model used by Electric Storage Battery Company, Yardney, Penna., with the exception that here also a closed system was adopted to eliminate the need for filling the cell with fresh electrolyte for each test.

3.1.1.3 A polarographic device for measuring the diffusion of zincate ion through battery separators

In strong potassium hydroxide solutions, dissolved zinc exists primarily as the zincate ion $[\text{Zn}(\text{OH})_4]^-$. The role of a battery separator with regard to diffusion of the zincate ion is not well defined. The function of the separator can hardly be to prevent the diffusion of the zincate ion from the zinc electrode throughout the electrolyte. Ordinary membranes based on cellulose or similar materials have relatively large diffusion coefficients for the zincate ion. Homogeneous distribution of the zincate ion throughout the whole cell must eventually occur. Nevertheless, since dendrite penetration may be related to zincate diffusion rate, diffusion measurements may be of value in understanding this phenomenon.

An instrument to make polarographic zincate determinations was constructed with a mercury dropping electrode as the sensing element; the construction is shown schematically in Figure 2.

Polarography in more concentrated potassium hydroxide has not been attempted previously. Since this is the region of interest in alkaline battery electrolytes, the dependence of the diffusion current on the zincate ion concentration had to be determined. With 40% KOH supporting electrolyte, a polarographic wave was obtained at the higher concentrations of the zincate, but none at very low zincate concentrations.

3.1.1.4 Electrolyte diffusion through separator membranes

Electrolyte diffusion through a separator should be connected to some extent with its electrical resistance. Additionally, exceptionally fast KOH diffusion might indicate numerous pinholes or cracks in the membrane, while very slow diffusion would indicate a sealed membrane. Therefore, measurements on several small areas can give information concerning membrane quality and uniformity.

The procedure adopted for electrolyte diffusion measurements consists of straightforward recording of OH^- ion concentration increase by pH measurements of initially pure water on one side of the membrane, with 40% KOH on the other side. Taking into account the parameters of the apparatus, the diffusion coefficient can be computed.

3.1.2 Organic Substrates

A large number of polymeric materials were tested for resistance to attack by aqueous 40% KOH, both at room temperature and at 135°C. The data obtained indicate that the following materials have sufficient chemical resistance to warrant consideration for battery separator construction:

- Teflon
- Polypropylene (Webril, Pellon)
- Polysulfone
- Polyphenylene Oxide
- Cast Epoxy (aromatic amine-cured)

Samples were evaluated as weighed 1-1/4 by 1-1/2 in. sheets in 40 ml Teflon-lined sealed cells containing 40% KOH, which could be heated to 135°C for 60 hours. The cooled, washed and dried samples were reweighed and measured. Representative data are given in Table I.

3.1.3 Inorganic Filler Materials

A large number of inorganic materials have been evaluated as ion-exchange fillers for use in composite separator membranes. An important prerequisite for any such material is that it have very limited

solubility in 8 M (40%) aqueous KOH solution, both at room temperature and at 135°C. Table II presents the solubilities of materials tested to date in 40% KOH, at room temperature. The compounds ZrO₂, TiO₂, SnO₂, ThO₂, MgO, as well as the molecular sieves Linde 4A and 5A, are relatively insoluble. Molecular weight gains observed for TiO₂ and MgO probably represent hydration with partial conversion to a hydroxide, under the conditions used. The data of Table II were obtained by tumbling one gram samples of dry weighed ion exchange material with 25 ml 40% KOH in closed polyethylene bottles for periods of 65 to 72 hours. The remaining solid was then filtered off, washed with water and dried at 110°C to constant weight.

The determination of solubility for these materials in 40% KOH at 135°C is much more difficult and only limited data have so far been obtained. Results to date indicate that at least 96% of ZrO₂ remains undissolved at 135°C. For barium zirconate 82.6% remained undissolved under the same conditions.

3.1.4 Polymeric Binders

A series of films was prepared both with and without zirconium hydroxide as a filler and with dimethylacetamide (DMAC) as the solvent for the polymer binder. The films were self-supporting. In other instances they were coated on Webril polypropylene mesh as a reinforcing structure. The following polymers were tried as binder: polysulfone, phenoxy, polyvinylidene fluoride, and polyphenylene oxide. All the films were carried through the prescribed sterilizing cycle in hot KOH solution.

The results can be summarized as follows:

(1) Polysulfone produced a mechanically strong membrane either unsupported or supported on Webril, with little weight loss and with preservation of dimensional stability.

(2) Phenoxy (Poron) has a low softening point which is around 100°C and stable films could only be prepared with a support of Webril.

(3) Polyvinylidene fluoride darkens in the cycling process, forming a brittle powdery film.

(4) Polyphenylene oxide polymer film was white, powdery and quite brittle.

As a result of these experiments, it was decided to use polysulfone in further separator fabrication. Polysulfone can be easily processed from a solvent solution and has the physical strength and chemical stability to withstand the cycling procedure. The incorporation of the filler caused no visible changes in behavior.

3.1.5 Membrane Fabrication

A large number of composite membranes were made up for evaluation of electrical characteristics. Specific details of construction are given in Table III. A typical procedure is described below.

A weighed 10 by 10 cm. square of 1.5 mil Webril polypropylene mat was used as the support material. This was saturated on both sides with a solution of 10 grams of a soluble polymer in 100 ml of an organic solvent. An excess of the powdered filler was applied to both sides of the wet mat and worked into the fabric with a glass slide. The resulting separator was dried in a horizontal position and weighed.

Since the necessary strength needed for the films used as separators was not achieved with the filler binder construction alone, it would seem necessary to support the film by a polypropylene web. If such a support is coated on the glass plate by an applicator, only one side is actually covered since the Webril rests on the glass. Also, during coagulation of the filler-binder mixture, only one side contacts the water and therefore this side seems to have different properties from the other. This can also be seen on microscopic cross section examinations. In order to coat the 1.5 mil Webril on both sides the equipment shown in the schematic sketch in Figure 3 was used. In this arrangement the Webril was drawn between steel shimstock knife blades. For the 1.5 mil Webril the blade opening was about 3 mils. The resulting thickness of film was about 2.5 mils when the latter was developed and dried.

The finished product could be put on a take-up roll after passing through the wash water. The speed of travel was about 1 ft./min. The coating mixture was supplied to both sides of the film from a funnel. Ball-milled mixtures containing 10, 12, 15, 20, 30, 40, 50, 60 and 70 g of Zr oxide in 15 g polysulfone and 100 ml DMAC were tried. Coating mixtures which contained 50 g hydrated zirconium oxide gave the best results in terms of the continuous coating technique. Table IV shows the resistivities of some of these films, fabricated using a polymer dissolved in a solvent as the binder plus a powdered inorganic filler, on Webril support. This table also gives the percent of polymer and filler, compared to the total weight of the resulting film. Polysulfone in DMAC was mainly used as the binding polymer solution. The fillers were zirconium oxide, titanium oxide, calcium oxide and Linde Molecular Sieve materials. As can be seen, some of these films fell into the required resistivity range (150 ohm-cm or 59 ohm-inch). Selected membranes were exposed to sterilization conditions without loss of permeability and without visible change in dimensions or appearance on microscopic observation. However, the distribution of filler material in these separators was non-uniform, as is evident from the photomicrographs shown in Figure 4. These inhomogeneities were also apparent from the considerable variations of resistance measurements.

3.1.5.1 Evaporation of solvent by heat

A number of membranes were prepared by casting on a glass plate. In this preparation method, the polymer solvent was evaporated by application of heat. It was soon noticed that such films are usually glossy on the side peeled from the glass plate and relatively rough on the side exposed to the air. Microscopic examination revealed a non-uniform distribution of the filler. Also, the average resistivity of even the thinnest films was too high to be acceptable and large variations were observed when the resistivity was measured at different places on the film. Sometimes resistivity values differing by a factor of three were noticed.

In order to reduce the resistivity, various amounts of cane sugar or polyvinyl alcohol solution were added to the binding resin solution. These materials were used as saturated solutions in DMAC. After drying in

an oven at 110°C, the films were then boiled in water to extract the soluble components. This procedure should produce a microporous structure which would be more permeable to KOH, thus decreasing the resistivity. Although the resistance of these films was, in general, slightly lowered, the soluble additives had an adverse effect on the distribution of the filler. Very often the filler separated into small islands, leaving regions containing no filler. For these reasons, other methods were tried for extraction of the solvent from the cast films.

3.1.5.2 Extraction of solvent by water and acetic acid

More satisfactory films were obtained by casting on a glass surface, and extracting the solvent from the still-wet films by immersion in an excess of water or dilute acetic acid. Films could be produced with, or without, filler. The films had an opaque milky appearance. The distribution of the filler remained quite uniform without any sign of segregation. The temperature of the extracting water was varied from 0°C to 90°C. The films did not form when the slide was immersed in very hot water, since the substance on the glass disintegrated before it coagulated into a solid film. On the other hand, the films processed in ice water were similar in appearance and resistivity to the ones produced in water at room temperature.

Films of even better appearance were obtained when the solvent was extracted with 50% acetic acid. These films were, on the average, somewhat thinner and had a glossy appearance even on the air side. They also had a lower resistance, in some instances, than did similar films produced by water extraction.

3.1.6 Membrane Properties

3.1.6.1 Effect of solvent on thickness and resistivity

A series of unfilled, water-extracted, polysulfone-DMAC films was prepared by casting on glass without any reinforcing support. The thickness of the wet film, as cast, was determined by the use of a Gardner Ultra Applicator. This device consists of a metal blade which slides parallel to the glass plate, and which can be set at definite

separation distances from the plate. Extraction of the film with water, followed by drying, would be expected to alter this initial thickness. The final thickness of films, after extraction and air-drying at room temperature, was investigated as a function of the Gardner blade setting and the initial polysulfone concentration in DMAC. It was shown that the thickness of the dry film is more dependent on the Gardner blade setting than upon the polysulfone concentration. Very roughly speaking, the dry films have about half the thickness of the Gardner blade setting.

It was also shown that less dense, more spongy films are apparently cast from the more dilute polymer solutions. Microscopic observations showed that the films prepared from dilute solutions consist of small cellular compartments, whereas those made from more concentrated binder solutions are seen to be more compact. Figure 5 shows a photomicrograph of the cross section of a membrane prepared without filler.

Some of the films obtained by the method just described were soaked in 40% KOH under vacuum and the electrical resistivity determined. The results are indicated in Figure 6. Here it can be seen that the solid to solvent ratio has a pronounced influence on resistivity. This indicates that the more dense films cannot soak up as much electrolyte as the less dense films apparently can. The resistance values were obtained with a 1/4" round aperture of 0.316 cm² area. Each point in the graph is an average of several determinations. The films formed from 10 g/100 ml solutions were relatively weak in mechanical strength, but unfilled films made with 15 g polysulfone had resistivity values much too high to fall into the acceptable region for battery separators.

When the solvent in the cast films is extracted with water, one obtains structures of a variable spongy nature, depending on the amount of solvent present. One would therefore expect the porosity of the binder to be affected by the solvent extraction process. Fast extraction could produce larger pores than slow extraction. During the extraction with acetic acid mixtures some influences of acetic acid concentration on the resistance of the obtained film was noted.

Another possible way to slow down the solvent extraction process would be to extract the cast film with mixtures of water and DMAC instead of pure water. A 50:50 (by volume) mixture of water and DMAC was therefore tried.

For these experiments, a mixture of 20 g MgO, 15 g of polysulfone and 100 ml DMAC was used after thorough ball milling for several hours. MgO was chosen because it should not possess any structural porosity of its own, so that the resulting porosity would be caused by the porosity of the binder alone. The Gardner blade was set to 8 mils for all the films reported. The films were cast on glass, and the solvent was extracted by immersion into the water-DMAC mixture for different lengths of time. Immersion times of 1, 10 and 1000 min. were investigated. In all cases a film was precipitated. After immersion in the water-DMAC mixture as specified they were further extracted by immersion in water. In this way all the DMAC was extracted, and stable films were obtained. The resulting films were hung up vertically in clips and dried either slowly for several days in air or dried in a shorter length of time in an oven heated to 120°C.

The result of these experiments is summarized in Table V. The resistance value is an average of 5 measurements at random places; so are the thickness values.

The result indicated certain trends. Shorter extraction times in the water-DMAC mixture seem to result in films with lower resistance. The resistance of films given 1000 min. extraction time was about 3 times that of films with extraction of 1 min. duration. Another trend seems to be noticeable; namely the oven dried films have considerably larger resistance (up to a factor of 5) than air dried ones. Since the thickness of these films when soaked in KOH is the same, this finding could indicate that oven-dried films have fewer or much smaller pores. One would expect, of course, that the pores shrink in the heat treatment when oven-dried.

3.1.6.2 Effect of filler properties and treatment on thickness and resistivity

Films were prepared by ball milling the filler with a 13% solution of polysulfone in DMAC. In these experiments, the same weight percent of filler was always used regardless of its composition. Figure 7 shows that the different fillers have only a secondary effect on the thickness of the film. Here again the resulting dry film thickness depended mainly on the blade setting, the dry thickness being again about half of that of the wet uncoagulated film on the glass slide.

Electrical resistivities for films containing fillers were determined. The films were soaked as usual in 40% KOH under vacuum for two days and in the wet form tested for resistivity. These films were first tested by an a.c. method. High resistance values were observed, which fell outside the limit of the apparatus. Surprisingly, much lower resistivity values (sometimes by a factor of 10) were obtained when the measurements were repeated, using the d.c. method. When the same films were once again measured with the a.c. resistance tester, values of resistivity were observed which were much lower than first observed by the a.c. method. This phenomenon was attributed to the pressure on the film. Since these films are pressed between flat flanges of considerable size, low resistance can be noticed over a wide area. That the pressure on the film is responsible for a decrease in resistivity was proven by pressing the film in a hydraulic press. Since the influence of pressure seems to change permanently the resistivity of the films, the following explanation could also be put forward. The walls of the tiny cells forming the spongy structure of the film, resulting from the fast extraction of solvent by water, might be permanently damaged by the pressure. If enough walls are broken, a more interconnected structure will be obtained, with a corresponding lowering in resistance. The relation of the magnitude of pressure to resistivity is described later.

Figure 8 represents the results with zeolon as filler. Films of different thickness were tested and usually 5 measurements selected for random areas of the film were made. While the points obtained are

scattered, showing a wide variation of resistivity from place to place on the film, there does seem to be a definite trend, namely that the resistivity increases with increasing thickness. Figure 8 also indicates that most of the values fall above the dashed line representing the limit of resistivity for the acceptable value of 150 ohm-cm.

Figure 9 shows the results for films prepared from titanium oxide as filler. Considerably higher resistances are found which deviate appreciably from the acceptable value of 150 ohm-cm indicated by the dashed line.

Somewhat better resistivities were obtained by using hydrated zirconium oxide as filler (Figure 10). The values are quite scattered but some of the averages fall below the prescribed limit of resistivity. An enlarged cross section of a zirconium hydroxide filled film is shown in Figure 11.

The resistivity of a film produced by spreading the filler and binder on 3 mil Webril is shown in Figure 12. Zeolon H was again the filler. These measurements do not show as much scatter as was observed for the unsupported films. All the measurements are below the limit set for the proper functioning as a battery separator. The thickness was measured several times and the limits are indicated by the line between arrows. The thicker film shows a variation of about 10%. Both resistivity and thickness were measured at random points.

3.1.6.2.1 Effects of ball milling of filler suspension

There are two kinds of voids intrinsic to the structure of the film. First, there are those due to the filler material, because of its internal structure, as in the zeolites, or resulting from the large amount of water of hydration in gel-forming filler substances. Second, there must be porosity in the binder, resulting in part from fast extraction of solvent and in part from places where the filler and binder do not completely fill the space. The porosity resulting from each of these contributions can have a different size distribution, so that the resistivity could be affected by any one of a number of parameters.

One question to be answered by experiment was the effect on resistivity of ball milling, since it can be assumed that ball milling affects the particle size of the filler.

To test this influence, hydrated zirconium oxide of 200 mesh (Biorad) was used. The mixture consisted of 20 g zirconium oxide, 15 g polysulfone and 100 ml DMAC. Films of different blade setting (6, 8, 10, 12 mil) were cast on glass and water extracted. These films were made after the mixture was ball milled for 20, 60 and 1000 minutes. The resulting films were washed in water overnight and dried. For resistivity measurements, the films were soaked in 40% KOH for 24 hours and the resistivity determined both as-obtained and after being pressed between Lucite plates at a load of 5×10^3 lb on the ram.

The extrapolated value for 5 mil thickness on the average film behavior was correlated against ball milling time. Figure 13 shows that longer ball milling gave a slightly lower resistance, but this difference is not large enough to be considered. One can conclude that the ball milling time, resulting probably in different particle size, does not have too large an influence on resistance. The fact that prolonged ball milling produces very uniform films is sufficient justification for this practice.

3.1.6.3 Effects of pressure on experimental separators

The resistance of composite films, composed of an inorganic filler and organic binder and processed by water extraction of the solvent, can be greatly and permanently reduced if these films are subjected to pressure. In order to gain some information of the relationship between pressure and resistance of films for their evaluation as battery separators, the following experiments were performed.

3.1.6.3.1 Methods of pressure application

The films were compressed between flat plates made of metal, Lucite or rubber sheets. The pressure was applied hydraulically. Most tests were carried out using Lucite flat plates. The films tested were

made from 10 g of filler, 15 g of polysulfone and 100 g of DMAC; they were precipitated by immersion in water and then soaked in 40% KOH for 24 hours.

3.1.6.3.2 Effects of pressure on resistivity of films

Figures 14, and 15 show the effect of pressure on the resistivity of ZrO_2 -loaded (10 and 20 g) films as a function of film thicknesses. The resistivity decreases with pressure, but this decrease is more gradual with 10 g filler. Quite an improvement can still be achieved in going from 5×10^3 to 10×10^3 lb load on the ram (Figure 14). This gradual decrease in resistivity is less pronounced with the 20 g filler composition (Figure 15), where a large drop in resistivity occurs at low pressures.

The pressure had another beneficial influence, namely the resistance measured on different locations on the film showed considerably less scatter, so that more uniform values are obtained on pressed films than on unpressed ones. In addition, the pressure effect is permanent.

Another approach is to press the membrane between two roller bars, which would lend itself best to large scale production of films having considerable size. However, it was found that the resistivity of films pressed between rollers is only slightly lower even after being rolled several times.

3.1.6.3.3 Effect of pressure on films with varied amounts of fillers

Figure 16 shows the behavior of the resistivity of films made with varying amounts of hydrated zirconia.

It can be seen that the resistivity changes rapidly with the amount of filler incorporated at low filler-loadings but becomes relatively insensitive to filler content at high loadings. The filler loadings above about 10 g ZrO_2 fall below the resistivity limit of 150 ohm-cm. Thirty grams of ZrO_2 could be a suitable content for a separator which gives a

filler-binder ratio of 2:1. The increase in filler of course weakens the film, but this is not of great importance if the membrane is supported (as, for example, on Webril mesh).

3.1.6.4 Behavior of membranes on sterilization testing

Selected membranes were cycled in 40% KOH at 135°C for 60 hours, and the results are shown in Table VI. These data indicate that in the sterilization process an almost complete filler extraction takes place.

The amount of filler remaining after cycling in hot KOH solution was determined by heating weighed samples of the membranes to a high enough temperature in air to destroy the organic matter. For comparison, samples of films which had not been exposed to hot KOH were also ashed. Additional companion runs were carried out on films not containing added filler. Data are given in Table VII. The results show that less than 0.05% ash remains from ashing the polysulfone alone, and about 0.5% residue is picked up from the necessary ball milling (porcelain No. 000 mill) used to mix polymer solution and filler. The residues remaining from filled membranes not exposed to hot KOH solution fall in the range 18 to 24% (from membranes containing 5 g filler and 15 g polymer). The fact that almost the entire filler material was extracted by the hot KOH solution during the cycling runs indicates that the film structure must be porous with little filler being completely encased in the polysulfone polymer matrix. But primarily the solution of the fillers in KOH was due to the large quantity of KOH used with respect to the amount of filler used. Therefore, by saturating the electrolyte with the filler, the loss of filler in the membranes was greatly reduced in general. The result of these measurements is summarized in Table VIII, where the results are compared to exposure of the same films in hot KOH not containing any of the excess amount of filler.

In cases where silver oxide was also present, there was a weight variation between the different samples, which appears to be from uneven deposition of metallic silver on the membrane. Some films had only dark spots, whereas others had a metallic appearance all over. The amount of

silver deposited on these films varied from 4% determined analytically as Ag to as high as 22%, taking into account the original weight of the sample. The deposited silver did not change the mechanical and physical properties of the films. Therefore, since the battery will apparently be sterilized in the discharged state, with only metallic silver present, no severe deterioration of the membrane is expected.

From these data we have concluded that hydrated zirconium oxide and titanium hydroxide appear to be the most resistant to extraction of the filler under sterilizing conditions. The Zeolon and Linde sieves show considerable solubility even with the filler-containing solutions.

3.1.6.5 Zn dendrite penetration through separators

It is well known that the successful application of the silver-zinc cell as a secondary battery was made possible by wrapping the silver and zinc electrode in cellophane, with several cycles obtainable through use of multiple layer wraps. Further extension of cycle life was achieved by limiting the discharge to less than 50% of battery capacity and by improving the composition of the separator. Modified cellulose or new permeable classes of resins were developed. These new materials are also more resistant to the degrading action of the silver oxides. The requirement for sterilization adds another factor to the still unsolved problem of dendrite penetration in the silver zinc storage battery.

Although not required by the contract, testing facilities were constructed to determine the resistance of membranes to dendrite penetration. The description of an instrument as given by Dalin and Solomon* was used as a guide in the present investigation. The test consists of determining the time necessary for the dendrite to develop a conductive path through the separator between the zinc electrode as cathode and a non-active sensing electrode in the form of a metallic net located on the other side of the separator. In the arrangement, a zinc electrode is also used as the anode, thus eliminating the depletion of zinc ions in the electrolyte

* J. E. Cooper and A. Fleischer, editors. (Air Force Aero Propulsion Labs. 1965). Chapter 12, "Zinc Penetration" by G. A. Dalin and F. Solomon.

solution during plating. Also, any effect of dissolved silver ions is avoided, which would not be the case if the test were to be made directly in a silver-zinc cell.

A high purity zinc sheet, abraded with fine steel wool, was used for both electrodes. The fine scratches should facilitate dendritic growth. In the design (Figure 17) the zinc area was marked out with a rubber spacer with a 3/4" diameter hole. In this way no edge of the zinc plate was exposed to the electrolyte. Usually enhanced dendritic growth occurs on an edge. Small holes were drilled on top and bottom of the exposed zinc surface. These holes were to allow the electrolyte to communicate with a compartment in back of the plate, and to permit the escape of any gas generated at the electrode surface. Since the zinc dendrites also grow on this side, opposite facing the anode, the surface was masked by painting with epoxy resin. Also, the holes were lined with polyethylene tubing to prevent dendrite growing on the edges.

The membrane itself was at a distance of 25 mils from the surface of the zinc plate, and in order to keep this distance, even with a separator which would crinkle in the electrolyte, the space was filled with a spacer of 25 mil glass mat of very high porosity. On top of the separator was placed a platinum net of 52 mesh gauze then another rubber gasket and a barrel filled with 40% KOH saturated at room temperature with ZnO. The anode was in the form of a cylinder. Visual inspection of the platinum gauze was possible. A high impedance electrometer (Keithley 200B) was used as the sensing electrometer for registering shorts between the zinc cathode and the platinum gauze. The output of the electrometer was registered on a recorder. The current through the cell was supplied by a well filtered variable voltage constant current power supply. The potential of the sensing electrode was between 0.5 to 1.5 volts. When a dendrite penetrated, a considerable voltage drop occurred. Very often this step was not well defined, but rather the voltage declined gradually over an appreciable time, or else had an oscillatory nature so that it was difficult to decide precisely when dendritic penetration had occurred.

It could be observed microscopically that the dendrites did not pierce the separator but grew into and inside of the structure. The pattern of penetration seems to be characteristic for certain classes of separators. In cellophanic separators the growth is at many points and the dendrites are relatively broad, whereas in the membranes with filler usually only a few points are penetrated and the dendrites are thin and hardly noticeable.

One purpose of this work was to reproduce the curve as given by Dalin and Soloman on page 41 of the stated reference. This curve represents the charge in coulombs necessary for dendrite penetration as a function of current density. The curve shows a quite sharp minimum. The current density at the minimum is recommended to be used for evaluation of the membranes. However, if this value is used, due to the steepness of the function at low current densities, a small deviation in current density could give a large deviation in the number of coulombs necessary for penetrating the membrane. Dalin and Solomon also state that the fact that this curve shows a minimum is significant to the probable shorting mechanism. It was therefore desirable to repeat similar measurements without and with a separator in order to evaluate the relation obtained.

It could be postulated that, as a first approximation, the number of coulombs/cm² necessary to produce a deposit which will reach the sensing electrode should be constant, regardless of the current density. Since only a certain space between cathode and sensing electrode has to be filled with the zinc, the amount should be expressed by $It/cm^2 = k$. That such a relation will not be realized stems from the known fact that the nature of the electrodeposited zinc, especially the habits of the dendritic growth, depends on current density. It was also observed that, probably due to density changes in the electrolyte, considerable more deposit is formed at the bottom of the small cell (3/4" diameter) than at the top, resulting in a quite uneven deposition. There might also be other reasons. For example, the nature of the zinc surface at the start of deposition will influence the time for the zinc growth to reach the platinum gauze.

The experimental values found, for the cell with only low density glass fiber felt as a spacer, are represented by the open circles in

Figure 18. The dashed curve represents the relation It/cm^2 drawn through the point at 25 mA/cm^2 . It can be seen that this relation seems to hold at low current densities and again at higher current densities. High current densities where an excess of hydrogen evolution is involved were not employed. Considerable deviation was observed around 15 mA/cm^2 . No interpretation of such a behavior will be given because duplicate runs show such a large scatter in the values, that many more points would be needed to gain any confidence in the results. The only relation indicated is that at high current densities a shorter time is needed than at low current densities to develop a bridge between cathode and sensing electrode. The fact that it requires only one dendrite to grow faster than the rest of the deposit, and since this growth seems to be rather unpredictable at present, a very large number of duplicate runs evaluated statistically would be necessary.

The same experiments were performed with a separator interposed. The separator was a Yardney colored cellophane for silver-zinc batteries. The result is shown by the solid circles in the graph. It can be clearly seen that the separator seems to have an influence, prolonging the time of developing shorts at low and higher current densities. The time necessary to penetrate the membrane between 10 mA/cm^2 and 20 mA/cm^2 does not differ substantially from the blank. But again, the statistical nature of such measurements must be considered. It would be premature to interpret the result.

The separators produced by water extraction of a filler and polysulfone as a binder were tested and are indicated on the graph at a current density of 20 mA/cm^2 . The points are scattered between the two previous curves. This would indicate that no drastic retardation of dendritic growth through these separators can be expected.

Some results were also obtained on a smaller cell of only 1 cm^2 area with 10 mil spacing between cathode and separator. These results again showed considerable scatter.

3.1.6.6 Silver ion diffusion

The determination of diffusion coefficients of silver through membranes by polarographic means has some advantages over other methods, in that the diffusion current is strictly proportional to concentration. The same instrument as described in previous reports for the zinc determination could be used.

There are some indications in the literature that silver can be determined polarographically using a dropping mercury electrode and dc polarography, although some difficulties can be expected. Polarography in concentrated KOH (40%) is virtually unknown, since for most polarography 0.1 M, or at most 1.0 M, solutions are used. The high concentration of KOH causes an increase in the background current.

A Sargent dc polarograph was used for this study. The dropping time of the mercury was 4 sec. The potential was applied against a large external Hg, HgO electrode, with the same concentration of KOH as in the main solution. Oxygen was expelled from the solution by prolonged bubbling of purified nitrogen through the supporting electrolyte. A sensitivity of 0.01 was chosen and maximum damping was employed. The sensitivity is expressed in $\mu\text{A}/\text{mm}$ chart length.

Monovalent silver dissolves in KOH to some extent. The complex formed is not known, but a dihydroxy or trihydroxy complex [for example, $(\text{Ag}(\text{OH})_2)^-$] might be present. In some previous work on silver determination, it has been noticed that the silver does not produce a normal polarographic wave, which would have its start from the background current of the supporting electrolyte. Actually, already at zero potential, the current starts below the zero line of the background current. This behavior has been attributed to the strong amalgamation tendency of silver and mercury. It was therefore of some interest to investigate the behavior in 40% KOH.

Curve (a) in Figure 19 represents the background current. Because of a large tank circuit in the (RC) line, the individual oscillations are smoothed out. Curve (b) represents the same 40% KOH to which a

drop of silver nitrate was added. After shaking for some time the filtered clear solution was used. The diffusion current is represented by i_d sat. when the solution was saturated with silver salt. Curves (c) and (d) were obtained by properly diluting the saturated solution with 40% KOH. Because the obtained curves are parallel in nature, they can be used for evaluation of the diffusion current by simply subtracting the background current, as indicated by the arrows on the graph. The point on the voltage scale where the evaluation is made is not critical because the diffusion current has a prolonged plateau.

Figure 20 was obtained by plotting the diffusion current against the different concentrations obtained by dilution of the saturated solution. The result is a straight line going through the origin, indicating that this method of obtaining diffusion current values is acceptable. This linear relation between silver ions in solutions and measured diffusion current can therefore be used for determination of silver diffusion through membranes.

As the silver ion supply, a saturated solution of silver oxide was used, freshly prepared by adding a drop of concentrated silver nitrate to the 40% KOH. One can assume the concentration on the silver side as constant, namely that of saturation at solubility of the silver oxide in 40% KOH at the given temperature. Figure 21 represents the relation between diffusion time and silver concentration in arbitrary units.

Silver diffusion through composite membranes (20 g filler, 15 g polysulfone in 100 ml DMAC) was investigated with Zeolon H and hydrated zirconium oxide as fillers. The films were water-coagulated and pressed under 5×10^3 lb pressure. The membranes were soaked in KOH for 12 hours before use.

The rate of silver diffusion through the membranes was much smaller than observed with cellophane by a factor of at least 10. The experiment had to run overnight (about 16 hours) in order to see any marked influence of silver on the diffusion current. Even so, the diffusion current was only 2.2% of the diffusion current obtained with a silver-oxide-saturated solution. If we

take the solubility of silver oxide in 40% KOH at room temperature as being close to 40 mg Ag/l, we get a diffusion rate of only 2.8×10^{-6} g Ag/cm² hours. This value represents a rather small amount of silver to be transported. Both membranes gave such small values.

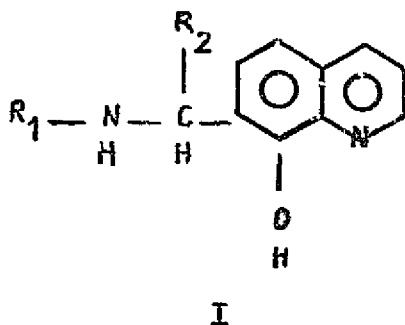
3.1.6.7 Tensile strength of films

Selected unsupported films and also coated Webril membranes were tested for tensile strength. Table IX reports these data. There is a decrease in both tensile strength and elongation in all samples after one exposure period in 40% KOH containing excess Zr(OH)₄ and Ag₂O. The exposure was 60 hours at 135°C.

There does not appear to be any great changes in strength in the unsupported film whether tested wet (water) or dry.

3.1.7 Chelate Modifications

The general approach emphasized in this phase of the work has been the incorporation of 8-hydroxyquinoline chelating groups into epoxy resin matrices. The intermediate Mannich bases I were prepared:



These compounds contain the 8-hydroxyquinoline moiety and in addition contain a side-chain secondary amine grouping through which molecule I can be bonded into the cured epoxy resin structure.

Compounds I are prepared from the interaction of the aldehyde R₂CHO, the amine R₁NH₂ and 8-hydroxyquinoline in alcoholic solution, employing prolonged reaction periods. Table X lists the compounds prepared together with some of the preparative details.

In the cured resin, linkage of the derivatives I to the resin matrix is through the side chain secondary amine grouping of I. Since the chelating agents I contain only a single secondary nitrogen, they are not efficient cross linking agents. We have, therefore, found it necessary to add m-phenylenediamine in order to obtain proper curing with the commercial Shell formulation Epon 826.

We have prepared two series of resins derived from the compounds I, which differ from each other in the relative amounts of I and m-phenylenediamine employed. Except as noted, good hard resins were obtained in each case after curing at 135°C.

Each of the resins listed in Table XI was tested for resistance to chemical attack in 40% aqueous KOH at 135°C for 60 hours. Samples were in the form of relatively thin flat fragments as obtained directly from the preparations. Weight loss after the treatment with KOH was taken as the criterion of stability, along with visible inspection. Most of the resins did not suffer obvious visible deterioration as a result of this treatment. In general, weight gains, rather than weight losses, were observed. We attribute these weight gains, at least in part, to the replacement of free phenolic groups (derived from I) in the resin by potassium cations, together with hydration of the resulting potassium salt groupings. Most of the resins of Table XI appear to be sufficiently resistant to attack by aqueous KOH to be used for battery separator applications.

Some effort was devoted to establish the presence of metal-binding capacity in some of the resins derived from the 8-hydroxyquinoline derivatives I. In the first series of experiments, a 200 mg ground sample of each resin was allowed to stand for one week in a solution prepared from 0.20 g cupric acetate monohydrate, 50 ml water, and a drop of liquid Aquet detergent, as wetting agent. The resulting solution (without resin) had a pH of 5.7. At the end of one week the solid was filtered off and washed with water, and was then ignited at 800°C to convert any copper content of the resin to CuO. For each of the resins investigated (Table XII), negligible residue was left after this treatment,

indicating that no appreciable uptake of Cu^{2+} had taken place. A possible reason for this lack of reaction may be the relatively low pH of the reaction mixture, since the parent compounds I are, themselves, known to require relatively high pH values in order to chelate with metal ions.

In a second series of runs the availability of the phenolic groups in the resin (derived from I) to ionization was investigated, since this is a prerequisite to chelation with metal ions. For this purpose, each 100 mg sample of powdered resin was allowed to stand overnight, at room temperature, with a mixture of 2.00 ml of 0.100 M aqueous NaOH and 50 ml water. The solid was then filtered off on sintered glass and washed with water. The filtrate (plus washings) was titrated with 0.02 M aqueous HCl to establish the amount of NaOH consumed by the resin. A glass-calomel electrode pair and a pH meter were used to follow the course of the titration. Results are expressed in Table XII as moles of OH^- consumed per mole of oxine derivative I present in the resin. (There was no conclusive evidence from the titration curves for the extraction of soluble acidic materials into the aqueous phase.)

For the compounds investigated (Table XII), the maximum possible value of the ratio (OH^- consumed/cmpd. I) is unity except for the first resin listed, where a value of 2 is possible, because of the additional presence of the carboxyl group. The values of the ratio observed (Table XII) are in all instances less than 20% of these values. This may be due to several reasons, including (a) interaction of a portion of the phenolic groups with the reaction mixture during the preparation of the resin, and (b) lack of complete penetration of the sodium hydroxide solution into the interior of the resin particles. The results do indicate, however, that a significant fraction of the phenolic groups in the cured resin remain available for further interaction with metal.

Battery separator membranes have been prepared containing, as fillers, epoxy resin particles derived from the 8-hydroxyquinoline derivatives I. Ten of these cured epoxy resins, derived from I, Epon 826, and m-phenylenediamine according to procedures described above, were incor-

porated into polysulfone films in a manner similar to the preparation of the films with inorganic filler. Specifically each gram of cured resin was combined with 3 g polysulfone resin and 20 ml dimethylacetamide. The mixture was ball milled for 16 hours with a porcelain 000 mill. The film was cast on glass using a Gardner applicator to establish the wet thickness at 7 mils. The film was then extracted with water and air-dried at room temperature in the usual fashion. The air-dried films were 3.0 to 4.6 mils in thickness. They have physical characteristics similar to those containing inorganic fillers.

On measuring the electrical resistivities of the films containing chelating epoxy resin fillers, the membranes showed the same sensitivity to applied pressure found in our previous work with inorganic fillers. In general, the resistivity values obtained for a particular applied pressure seem to be insensitive to the nature of R_1 and R_2 in formula I. Table XIII lists the resistivity data for each of the films studied.

3.1.8 Conclusions from First Phase

At the end of the first part of this program, which was devoted to the screening of numerous ingredients and of several methods for making sterilizable battery separators, the following conclusions were reached:

a) A reasonable approach to solving the problem involves membranes which behave similarly to cellophane as far as porosity and osmotic character are concerned, but which withstand the prolonged action of hot caustic and also retard dendritic growth. Such separators possessing the necessary porosity and thickness could best be fabricated by making heterogeneous composite membranes consisting of inorganic filler or fillers bound by an organic binder, and supported by an organic-type tape. Such a system could be realized in the form of flexible membranes of the desired thickness, preferably consisting of multilayers of thin membranes. The composite would acquire the required porosity by suitable manipulation of the organic binder, while the filler, consisting of very

small particles, would have the property of soaking up enough electrolyte to impart the necessary conduction to keep the resistivity within the required limits.

b) The most promising binder is a polysulfone polymer, such as polysulfone 1700 by the Union Carbide and Carbon Company, which is resistant to the attack by concentrated caustic.

c) Hydrated zirconia and some zeolites exhibit satisfactory resistance to hot caustic and contribute to the acceptable electrical properties of the composite membrane.

d) A supporting substrate almost impervious to hot, concentrated KOH is found in the class of polypropylene felts.

e) The best method for making separator materials of good porosity consists in the coating of the polysulfone :filler : solvent mix on to polypropylene tape, followed by extraction of the mix solvent and coagulation of the polysulfone by means of immersion in water or acetic acid solutions.

f) Silver ion penetration (measured by polarographic methods) through membranes made as above is small.

g) Zinc dendrite penetration through such membranes is difficult to measure, but indications are that these membranes do not retard dendrite growth appreciably.

h) Compression (up to 10^4 lb/sq. in.) of wet membranes decreases their resistance by a factor of 10.

i) The exploitation of all the above mentioned facts has resulted in experimental membranes whose specific resistivity values fall below the specified maximum limit of 150 ohm-cm, exhibit fast electrolyte flow and are reasonably resistant to the attack by hot concentrated caustic.

j) The difficulty of making chelate-modified resins to be used as ion-exchange fillers and their modest properties do not warrant any further work in this direction.

3.2 SECOND PHASE

The second phase of this contract involves the choice of one of the most promising systems studied in Phase 1, improvement of the chosen system and the establishment of criteria, methods and procedures for the semi-industrial fabrication on a continuous scale of one-foot wide sterilizable battery separator material. The greatest portion of the work was devoted to the latter goal.

3.2.1 Test Equipment

The resistance tester used was a d.c. conductivity bridge Model 31 made by The Yellow Spring Company and connected with the same type of cell as described in 4.1.1.2. This tester was very accurate and could be used over a wide range of resistance values.

The method of analysis used for the determination of silver ion diffusion through the membranes was that of polarography. It was found, however, that this method did not lend itself to the measurement of zincate ion diffusion, which was instead measured by flame absorption spectroscopy. Both methods are discussed in more detail in the appropriate sections.

Electrolyte flow was determined as explained in 4.1.1.4.

3.2.2 Organic Substrates

On the basis of previous findings it was decided to make separator materials consisting of a supporting tape coated by a polymer: inorganic filler: solvent mixture. The tape initially chosen was Webril 3 and 12 inch wide tape (Kendall Fiber Product Division), which is a non-woven polypropylene fabric with a nominal thickness of 1.4-1.5 mils. This material seems satisfactory from the points of view of strength, porosity and coatibility.

Irregularities in diffusion rates and resistivity values, however, were observed frequently, and the doubt arose as to whether the thickness of the Webril tape is as constant as claimed. It was found that the thickness varied from a minimum of 1.4 mils to a maximum of 2.1 mils, with high and low values frequently very close to each other, and no particular

concentration of high or low spots. New tape batches had more constant average thickness, but closer to 1.9 mils than to the originally claimed 1.4 mils. Since these tapes were machine cut, their edges were smooth, even and free of visible stresses.

However, in general Webril tapes were distinguished by very rough weave and by large and irregular voids, so that the coating mixture has more difficulty in covering over these substantial holes. Thus, pinholes resulted. In addition, heat shrinking was very pronounced (about 1/8 inch over 3 inches of original width). This may have been due to the fact that some of the polypropylene yarn supplied is of coarser denier; this results in thicker but coarser tape.

Some new materials were received and tested. From Union Carbide were obtained very small samples of their new and very expensive yttria-stabilized zirconia cloth, with nominal thicknesses of about 15 mil. These samples appeared to be relatively weak mechanically, and to be filled with some powder or dust. They were immersed in 40% KOH for 2 days; when they were taken out of the caustic for resistivity measurements, it was found that their mechanical strength had diminished further, to the point where they could hardly be handled. Only one sample could be tested for resistivity; all the others had practically disintegrated in the KOH. As it appears now, this material is too fragile for our purposes.

DALKASEP film was received from Dewey and Almy; who reported the intention of manufacturing it in continuous lengths if it becomes commercial. This material consists of microporous polyethylene designed for use as separator in alkaline batteries, particularly silver-zinc batteries.

Samples of DALKASEP underwent standard sterilization cycle (60 hours in 40% KOH at 135°C). At the end of the test the samples had shrunk drastically, losing about 80% of their original area. Conversely, their thickness had increased two fold. Their resistivity before sterilization cycling was too low to measure on our meter; after this cycling the samples were too small to fit our resistivity cell. In addition, the weight of the samples after sterilization had increased fifty percent, probably indicating a

chemical reaction with the caustic. These results indicate that this material does not lend itself to use as battery separator material which must be able to withstand a temperature of 135°C in 40% KOH.

Two polypropylene substrates, Pellon styles 2530 and FT 2140, were tested for resistivity and electrolyte flow properties. The thickness of the former was 6 mils on the average, while the latter averaged 7 mils. They both looked uniform in their felt-like structure but were soft and compressible.

Tape style 2530 offered negligible resistance to KOH passage (pH 14 in 1.5 minutes) and exhibited a specific resistivity of 10 ohm-inch. Style FT 2140 tape had higher electrolyte flow resistance (pH 14 in 25 minutes, 13.5 in 2.5 minutes) and a specific resistivity of 23 ohm-inch. Several rolls both 3 and 12 inches wide were obtained from the Pellon Company.

Webril EM 476 (ave. thickness 0.0027 inch), both in 3 inch and 12 inch wide tape was obtained; this material was claimed to have a fuller structure and to be stronger than E 1403. Samples of polypropylene (AFCO Fentron) were obtained from the American Felt Company. They were much too thick for our application (0.040 to 0.065 inch).

Pellon 2530 appeared to be impregnated with a sticky substance which made its travel around the rollers of the tower difficult. In addition, it stretched considerably and was rather soft. In general, Pellon 2530 did not seem to be suitable for tower coating.

3.2.3 Inorganic Fillers

Inorganic fillers were chosen to act both as reinforcing agents and as porosity foci; on the basis of previous work the most promising inorganic filler was hydrated zirconia supplied by the Bio Rad Company in 100-200 mesh particle size (H2O-1 ion exchange crystals). Some 20-50 mesh zirconia was sent by the same company, and this material, which loses 20% of its weight on heating for 20 hours in runs at 110°C, was successfully used in several formulations.

Another type of zirconia was purchased and tested, namely "special" hydrous form ZrO_2 from the Titanium Alloy Division, National Lead Company. This filler contained a large amount of absorbed water; in fact 38.5% of the filler's weight was lost after heating for 18 hours at 180°C in vacuo. The TAM zirconia as well was used successfully as a filler in separator coating formulations. Zeolon H pigment was also used satisfactorily in coating formulations (weight loss is 11.1% after heating at 120°C for 18 hours); however, in view of the fact that Zeolon H was found to be more soluble in concentrated caustic than hydrated zirconia, the work done using Zeolon was mainly carried out for practice and to settle some procedural points.

It must be noted that drying of any of the fillers mentioned above, and prolonged ball milling in the presence of the binder solution, are of paramount importance if one wishes to obtain smooth coatings of reproducible quality.

3.2.4 Polymeric Binders

The polymer used previously with best results as a separator binder has been a polysulfone (Pl700) supplied in pellet form by the Union Carbide Company. The structure of this material consists of aromatic rings connected to each other by ether, isopropylidene and sulfone linkages. While the sulfone and ether links are known to be resistant to thermal and oxidative attack and to the attack of concentrated alkali, the isopropylidene group constitutes a weak point in the polymer chain in this respect. Therefore we acquired samples of polysulfone (polymer 360) from the 3M Co.

which consists of a chain with ether, sulfone and diphenyl linkages without the relatively labile isopropylidene group. This material is supplied in pellet form of two sizes (360 and 361).

Attempts were made to dissolve those resins (361 as a free flowing, fine powder and 360 in the form of granules) in DMAC. At a solids concentration of about 13% neither dissolved easily nor completely. At 9% solids concentration Polymer 360 did not dissolve completely, and left a considerable amount of whitish, dusty residue. However, Polymer 361 dissolved almost completely at this concentration, and the solution was considered suitable for testing.

3.2.5 Wetting Agents

The formulation of the coating mix generally consisted of 3:1 20-50 mesh oxide: polysulfone in DMAC; however, in some cases wetting agents were added in varying proportions. For example, Alkaterge E was added in 0.5, 1.0 and 2.0 percent ratios, on the basis of solid weight, to mixes of different viscosities. The best results were obtained in the cases where the Alkaterge E was added in the proportion of 1%.

3.2.6 Apparatus and Procedures

3.2.6.1 Hand-coating device

The coating device for screening purposes consisted of two stainless steel shimstock blades set edge on edge at a predetermined distance from each other and secured by screws to a common handle. The piece of Webril is inserted in the gap between the blades and is held in a vertical position; several portions of the coating mix are poured on the blades on either side of the handheld Webril sample, which is then pulled down slowly and evenly. This action causes the Webril tape to be covered on either side by a smooth, even coat whose thickness is determined by the gap between the blades. It is of paramount importance that: (1) the coating mixture be continually agitated to prevent settling of filler (this is usually done magnetically); (2) that new coating mixtures be made frequently in order to avoid problems due to evaporation

of solvent; (3) that after each coating the blades and the gap be cleaned carefully, since the polysulfone resin easily solidifies out of solution thereby causing rough coatings on the next sample.

The procedure mentioned above, laborious though it is, did supply coated samples of relative uniform thicknesses possessing good continuity. It also circumvented the drawback of different surfaces as in the case of films cast on glass.

3.2.6.2 Laboratory-size continuous coating apparatus

Figure 22 shows a sketch of the experimental continuous coating machine. The whole set-up is an improvement over that of Figure 3; it is mounted on a supporting frame which is fastened to a movable platform. The support tape 3 is wound around the payoff roller and is kept under tension by a friction brake 2. The tape then passes through an arrangement consisting of an 8 inch long Gardner film casting knife 5 and a 9 inch long aluminum angle 6 one edge of which is butted lengthwise, at an angle, against the edge of the Gardner applicator's knife. This set-up serves to adjust with some accuracy the gap through which the tape slowly travels and which limits the amount of binder:filler:solvent mix 4 to be deposited on the tape.

The coated tape then dips into tank 8, being led parallel to the bottom of the tank by two 1/2 inch Teflon guide rods 7. The tank is filled with the appropriate solvent mixture which precipitates the organic binder out of its DMAC solution and, at the same time, extracts the DMAC solvent thus causing porosity to be formed in the binder:filler layer. The position of the two rods 7 relative to each other is one of the many parameters governing the duration of the dip of the tape and, therefore, the degree of porosity of the separator.

The treated tape then leaves tank 8 and travels between two rollers 9 the gap between which can be adjusted. Thus pressure can be exerted continuously upon the composite to improve its conductivity. Finally, the treated separator tape is rolled up by a 2 inch diameter take up roller driven by a high torque, low speed motor. Heaters were

installed on either side of the tape halfway between the compression rollers 9 and the take up roller 10, and a circulating pump equipped with filter has been installed at tank 8. On a large scale operation consideration should be given to monitoring the composition of the solvent mixture in the tank so as to keep the ingredient proportions constant.

3.2.6.3 Methods for application of coating mixture to supporting tape

Drawbacks were constantly encountered in the course of coating experiments carried out using a temporary laboratory coating tower which employs a Gardner knife applicator; they were due to the fact that the zirconia:polysulfone:DMAC mixture was difficult to apply evenly and uniformly onto the tape mainly because the blade alignment was hard to maintain and because the two knife blades acted as collectors or filters for the solid oxide. Ultimately, the coat applied to the tape possessed a different composition from that of the original coating mixture.

Therefore, a dip-coating method was tested as follows: the laboratory tower was modified by the installation of a dip-pan equipped with a freely moving roller, two wiper rods (which originally were grooved pins, and later were replaced by more efficient Teflon rods one half inch in diameter). A vertical six foot high furnace was installed: it was heated by strip heaters and heating lamps to a temperature that never exceeded about 50°C. Experimental runs were made with and without a coagulating and extracting bath; it was found that the absence of the bath prevented the coated tape from drying properly in the vertical oven.

Several continuous dip-coating runs were made in which the ingredient ratios in the coating mixture were varied to check the effects of viscosity and solids contents. The coating mixture needed to be agitated thoroughly in order to prevent inhomogeneous coatings, but care had to be taken to eliminate sources of pinholes in the coated tape. Coating speeds ranged from 0.5 to 7 feet per minute; at the latter speed the coated tape emerged wet from the oven.

The best results were obtained at a speed of 3 ft/min.; the resistivity of the samples from this run (3:1 oxide:PS) was of the order of 70 ohm-inch and the electrolyte diffusion rates were acceptable (12.5 pH units after 30 minutes' exposure). In general, the thickness of the coated tape remained constant, but there occurred some shrinking across the tape.

On the basis of the results obtained in this set of experiments, it was decided that dip-coating was a promising method for manufacturing sterilizable battery separators in a continuous manner.

3.2.6.4 Continuous dip-coating in industrial coating tower

Reasonably successful coatings of 3 inch wide Webril tape using a dip-coating method and an experimental, laboratory size coating tower led us to attempt the scaling up of this process. To this purpose a semi-commercial metal foil coating tower was modified to accept our coating conditions.

Several continuous runs were made on this tower to investigate some parameters, such as viscosity of mix, oxide:polysulfone ratios, and coarser versus finer zirconia. On the basis of coatability, the best combination appears to be, at present, that containing a 3:1 oxide:PS ratio. Best results were obtained at a speed of 3.0 - 3.5 ft/minute. The oxide used here was the 20-50 mesh zirconia. Even in this type of run, however, there was shrinkage across the coated tape which resulted in creases running longitudinally. The open weave of the Webril tape was probably responsible for the creasing.

The final mechanical arrangement consisted of a pay-off roller from which the tape proceeds to two driving rollers; then the tape is dipped in the pan containing the stirred coating mixture and runs between two 1-inch Teflon wiper rods. It subsequently proceeds over the top wiper rod at a very sharp angle, down into the water:dioxane bath, around a roller at the bottom of the bath, up through the oven and then on to the wind-up rollers.

This arrangement is reasonably satisfactory for screening purposes. However, the stirring of the mixture is insufficient. In addition, the various angles assumed by the tape in its course were increased to reduce tape stretching. This temporary setup worked only with 3 inch wide tape, so that provisions were made to replace it with one able to accomodate foot-wide tape as required by the contract.

Coating supporting tapes using a dip tank and wiper rods had proven to be the best method tried. However, because the coating mixture is a slurry, an efficient means of agitation was necessary to prevent the inorganic filler from settling out. This problem was solved by redesigning the dipping tank so that a circulating pump could be included.

In order to reduce the amount of tape shrinkage at the temperatures used to give a dry coated tape, the vertical drying oven was doubled in length. This resulted in higher coating speeds at lower temperatures giving dry coated tapes with little or no shrinkage.

Most of the work was done using 3" wide supporting tape. Several runs were made with 12" wide tape and these showed the need of modifying the take-up system because, with rollers being only 12" wide, the tape continuously overlapped them. Also better roller alignment was necessary because the web-guiding system did not work. This is controlled by a light beam and the coated tape was transparent to this beam. A pneumatic web-guide, or curved spreader rollers would probably obviate this problem.

As requested by the contract, samples of one foot wide battery separators must be supplied. Thus the coating tower used to coat 3 inch wide tape was modified to accept 12 inch wide tape; new, larger and improved dip and coagulating tanks were constructed, together with longer driving and take-up rollers (Fig. 23).

3.2.7 Formulations

Most of the coating formulations reported here were made using polysulfone solutions consisting of 15 g of polysulfone per 100 g of DMAC. The dried oxide is generally added to the solution in 20:15, 30:15, or 45:15 ratios (or 1.33:1, 2:1, and 3:1) between the filler and the solid polymer, and the whole ball milled. For example, a formulation may consist of 80 g of dried zirconia in 460 g of polysulfone solution (containing 60 g of the binder), so that the filler:binder ratio in this case is 20:15 (or 1.33:1). This amount of material is generally sufficient for one continuous run of several dozen feet; however, when experimental runs are longer, the practice has been to use fresh batches used consecutively because the solvent is very hydrophilic and exhibits a relatively high vapor pressure, thereby causing the premature precipitation or coagulation of the PS binder.

3.2.8 Membrane Properties

3.2.8.1 Effect of extraction time

The manner in which the coated tape acquires its porosity is envisioned as being a result of a capillary extraction of the solvent, originally present in the coating mixture, by an extractant solution. A simultaneous effect of the immersion in the extracting bath is the coagulation or precipitation of the organic binder to give a polymeric coating which appears continuous to the naked eye.

Since the porosity acquired by this method is also dependent on the type, concentration, particle size or the inorganic filler, it is conceivable that both time of immersion and type and concentration of extracting solutions have a bearing on the resistivity and ion diffusion characteristics of separator composites.

Therefore, the effect of time of extraction in several types of extracting solutions, as evidences by the variation of resistivity and ion diffusion values, was investigated as follows:

After the Nubril samples were coated as described in 3.2.6.1, they were extracted for the required length of time in predetermined extractant solutions. At the end of the extraction time the coated

samples were dried gently between sheets of absorbent paper, and their thickness measured.

Each extraction run was made in duplicate and the shim stock blade gap chosen was 3 mils.

Below appears the schedule followed for the investigation of extraction time effect:

1. Time of Extraction: 1 minute, 30, 120 and 360 minutes

2. Extraction Solutions (by volume)

50:50 Water:DMAC

25:75 Water:DMAC

75:25 Water:DMAC

50:50 Water:DMSO

25:75 Water:DMSO

75:25 Water:DMSO

50:50 Water:Dioxane

25:75 Water:Dioxane

75:25 Water:Dioxane

50:50 Water:Acetic acid

25:75 Water:Acetic acid

75:25 Water:Acetic acid

Some samples were coated and air dried (instead of being extracted) to be used as standards.

These experiments were carried out on samples made using Zeolon H as a filler (Zeolon H:Polysulfone:DMAC = 20:15:100), coated on nominal 1.5 mil Webril tape, and on samples made with 20-50 mesh Bio-Rad Zirconia (80 g ZrO_2 , 460 g of 15% PS:DMAC solution, oxide:PS ratio = 20:15) on the same Webril. The parameters studied were specific resistivity and electrolyte diffusion time as functions of time of extraction and nature of extractant.

In the case of the electrolyte diffusion time it was found that the separator samples prepared as mentioned above were free of gross defects (see typical pH: time curve as compared with bare Webril and FUDO cellophane,

Figs. 24-26) or imperfections which would allow extremely fast electrolyte diffusion. But, on the whole, there seems to be no clear correlation between electrolyte diffusion and extraction times or solutions. The samples with fast electrolyte diffusion are also the ones with best resistivity values.

The results of the extraction investigation may be summarized as follows:

- a. Dioxane - containing extracting solutions, especially the ones in which the dioxane is the preponderant ingredient, yield battery separator composites (containing both Zeolon H and Bio Rad zirconia) which have shown the best resistivity and ion diffusion-values. This indicates that the pore size and distribution of these materials are fairly uniform.
- b. Time of immersion does not seem to be an important factor in the preparation of satisfactory separator material. This may be due to the fact that the coagulation and solvent leaching actions are fast and simultaneous.
- c. Air-dried samples coated with the formulations used in the investigation of the effects of immersion times generally show good resistivity and KOH diffusion values.

3.2.8.2 Effects of variations of oxide loading

This set of experiments was carried out using the laboratory size coating tower equipped with Gardner knife spreaders. The formulations involved oxide:polysulfone ratios of 3:1 and 4:1 by weight. The oxide used here was oven-dried Bio-Rad. Specific resistivity values and electrolyte flow values were used as criteria. The results indicated that higher oxide loadings result in faster electrolyte diffusion and lower resistivity; the coatings, however, are not as flexible as the ones made using lower oxide contents, and are prone to cracking. The best results are obtained at a 3:1 oxide:polysulfone ratio, at coating speeds of 3-4 ft/min. Typical specific resistivity values involved in the 3:1 oxide:PS case ranged from 70 to 158 ohm-cm, at thicknesses varying from 4.2 to 5.3 mils of coated tape and at coating speeds of 3-4 ft/min. The samples with a 4:1 oxide:PS ratio gave specific resistivity values ranging from 100 to 1000 ohm-cm at average thicknesses of 4 mils and at speeds of 3-4 ft/min. Ball milling the coating mixtures for several days generally resulted in smoother coatings and better filling of the Webrii tape voids.

3.2.8.3 Effect on resistance of time of soaking in KOH

The effect of KOH soaking time on resistance of experimental separator materials was studied next. The sample used was made from a 3:1 oxide:PS mix; it was soaked for 24 hours in KOH and then tested using the coarse conductivity bridge. This measurement gave a resistance value of 280 ohms. The same piece was tested with a new, more precise meter (YellowSpring Co., Model 31), which gave a resistance of 300 ohms. It was then placed in the resistivity cell in the presence of 40 percent KOH and its resistance measured as a function of time (see Fig. 27). The results show that, in the case of the relatively thick sample, prolonged exposure to 40 percent KOH brings about a decrease in resistance of more than one order of magnitude. This implies that lower resistivities than expected might be encountered in a battery after some actual operation time. In addition, these experiments indicate that it would be advisable to soak all samples at least 48 hours in order to arrive at meaningful, steady resistance values.

3.2.8.4 Sterilization tests

The resistance to sterilization in hot concentrated caustic is of paramount importance. While fillers and some substrates were tested in Phase 1, some more ingredients were tested under the conditions set down below.

The samples from separator materials which were obtained at several speeds from each coating run, were cut to 2 x 1.5 inch size and sterilized in 40 percent KOH for 60 hours at 135°C. The coating runs from which the samples are derived are identified in Table XIV.

The containers, in which the samples to be sterilized were placed in contact with 40 percent KOH, were stainless steel cups with Teflon liners. They were sealed by steel covers, Teflon washers and C clamps, and exposed to heat in a box containing sand. The procedure and the apparatus involved are described in detail in the First Monthly Report of this contract.

The effect of hot caustic sterilization on separator membranes was measured in terms of:

1. Specific resistivity before and after sterilization.
2. Weight before and after sterilization.
3. Thickness before and after sterilization.

A sample of a new Webril fabric batch claimed to be more uniform than earlier types, also underwent the sterilization cycle, mainly to determine its weight loss. Since it was found that the polysulfone PS 1700 weight loss from sterilization was negligible, it was assumed that the weight losses observed in this work were due only to the dissolution of the oxide and of the Webril into the KOH. By determining how much weight Webril would lose, the oxide weight loss could then be determined. It must be noted, however, that the resistance of polysulfone 361 to hot caustic was not determined, but it was assumed to be as negligible as that of PS 1700.

Table XV gives the results of the sterilization cycle of a total of 16 coated samples (see Table XIV) and of plain Webril.

The data shown in Table XV indicate that Polysulfone Polymer 361 is not suited for use as a binder in battery separators which must withstand attack by hot, concentrated caustic. Indeed, samples from C58-29-1 down, all containing PS 361, lost all their coating as indicated by their elevated weight losses and reduction in thickness after sterilization. KOH damage was also demonstrated by the presence of yellow color both on the separator sample and in the KOH solution, after sterilization. However, this color could be washed off the samples, which then resembled very closely the original, plain Webril tape. The thickness values after sterilization indicated very strongly that all that remained was Webril, and that the coating mixture went completely into solution.

The situation was quite different in the case of the coating mixtures containing polysulfone P 1700. Here the thickness of the coated samples before and after sterilization remained generally constant and no change was detected in the separators after sterilization. In some cases the sample resistivity readings were so close to the blank readings that no values were recorded. The weight losses were fairly constant at around 8-9 percent, from which the weight loss exhibited by plain Webril should be subtracted. If operation of the sterilizable battery can withstand it, saturation of the KOH

solution with free zirconia would probably reduce the weight loss of separators. In any case, this level of weight loss might not be significant in terms of resistivity and mechanical characteristics; it might, however, be important with respect to silver and zinc ion diffusion.

3.2.8.5 Effects of different oxide loadings and concentrations of wetting agents on sterilization results

Sterilization Table XVI shows the results of exposing samples of six continuous runs (C58-43-1, -53-2, -56-1(A), -57-1 and -58-1), and of five new Webril fabrics, to a sterilizing cycle consisting of 60 hours immersion in 40% KOH at 135°C. The table immediately below shows the compositions involved in the above mentioned runs.

Identification of Samples for Resistance to Sterilization Tests

<u>Sample No.</u>	<u>Oxide*:PS Ratio</u>	<u>Solids Content</u>	<u>Additive</u>	<u>Oxide Mesh</u>
C58-43-1	2	10.7	--	20-50
C58-44-1	3.5	14.9	--	20-50
C58-53-2	3	14.9	1% Alkaterge E	20-50
C58-56-1A	4	14.9	1% Alkaterge E	100-200
C58-57-1	3	14.9	0.5% Alkaterge E	20-50
C58-58-1	3	14.9	2% Alkaterge E	20-50

* The oxide was Bio-Rad Zirconia, 20-50 mesh

In the case of the coated tapes, in general, sterilization brought the resistivity values down, in many instances below the top permissible resistivity limit (about 60 ohms-inch). The weight losses averaged 10% and most of the coated samples were not physically affected by the sterilization step; thickness of samples before and after sterilization also seemed relatively unchanged.

In addition, the samples obtained from mixtures containing 1% Alkaterge E (an amine type wetting agent) exhibited relatively low resistivities both before and after sterilization, although their weight losses were slightly higher than normal. This may have been due to yet another change in the quality of the Webril tape.

All the plain Webril samples exhibited low weight losses, comparable to those sustained by the first obtained Webril samples under the same conditions. In a few cases the thicknesses increased after sterilization especially in the case of H739 and H751. It was thought that some swelling liquid had been retained by the samples after washing and drying; however, prolonged drying did not reduce the thickness values measured after sterilization nor did it increase the weight loss. This probably means that the Webril fibers were permanently rearranged by the KOH treatment. The yellow-green color present in the KOH solution after sterilization, and the curling of the samples may indicate the presence of bonding agents in the non-woven Webril. Four of these new tapes were so tightly made that they showed some resistivity even without being coated. The results of the sterilization cycle on the new plain Webril tapes, some of which are too thick, lead us to the conclusion that the tape used until now may be satisfactory, even though it is of a coarse grade.

3.2.8.6 Determination of silver ion diffusion through membranes

A continuous method of silver ion determination was required which would not involve a change in the volume of the solutions under study. The method of analysis chosen was that of polarography. The instrument used was a Heath built polarograph, model IUW-402 M employing a dropping mercury electrode (DME) as the working electrode and a massive, external mercury-mercuric oxide electrode (in 40% KOH) as the reference and counter electrodes. This allows one to scan from 0 v to -1.5 v with respect to the counter electrode. The cathodic step due to silver ions coincides with the limiting value of the polarogram, arising from the anodization of mercury.

The limiting or diffusion current for 40% KOH is 0.025 μ A. With silver ions dissolved in 40% KOH, the diffusion current increases linearly with increase in silver ion concentration. A saturated silver solution was prepared by dissolving silver nitrate in 40% KOH. After filtering, portions of this solution were diluted to different extents with 40% KOH. Each solution was analyzed by a 'wet' chemical method and a polarogram also obtained. The chemical analysis was carried out as follows: the sample was acidified to

0.1N with respect to nitric acid. The silver was extracted with dithizonate in carbon tetrachloride. The excess dithizonate was removed from the carbon tetrachloride with dilute ammonium hydroxide and the determination was completed by spectrophotometric measurement of the residual silver dithizonate colors.

The following results have been obtained:

Calibration of Polarograph for Detection of Silver in 40% Caustic

<u>Sample</u>	<u>Silver Content by the Dithizonate Method, p.p.m.</u>	<u>Silver Content Less Blank, p.p.m.</u>	<u>Diffusion Current, 10² μA</u>	<u>Diffusion Current Corrected for Blank 10² μA</u>
40% KOH blank	0.9	---	2.5	----
Silver sol. 1	3.8	2.9	15.1	12.6
Silver sol. 2	9.6	8.7	20.6	18.1
Silver sol. 3	23.4	22.5	35.8	33.3
Silver sol. 4	51.3	50.4	63.5	61.0

Several samples of battery separator membranes, which were previously found to have a satisfactory resistivity and sterilization properties, underwent tests to measure polarographically the flow of silver ions through them as a function of time. Special cells were used to contain the concentrated KOH:Ag solution.

Measurements were carried out continuously over a period ranging from 44 to 140 hours for each membrane sample which was placed between two Teflon cells, one containing the known Ag solution in 40% KOH and the other straight 40% KOH. The runs were made under a blanket of N₂ to prevent formation of potassium carbonate.

The results of this series of experiments were: of six samples tested, five had negligible Ag ion flow after no less than 45 hours of exposure to a saturated KOH-Ag solution; in fact, one lasted 140 hours without perceptible ion flow. A sixth sample showed the passage of 35 ppm Ag after 118 hours, but it took about 48 hours to show the passage of only about 4 ppm of Ag.

3.2.8.7 Determination of zinc ion diffusion rates

Preliminary experiments have shown that the measurement of the zincate ion cannot be carried out satisfactorily by polarography. The half-wave of the zincate ion occurs very close to that for the reduction of water. In practice, a characteristic zincate plateau was difficult to identify in 40% KOH. Further, in solutions containing very small amounts of zincate ion, of the order of 15 parts per million, no such step was observed.

Therefore, analyses for zinc ion diffusion was carried out using flame absorption spectroscopy.

The apparatus consisted of two Teflon cups (2" I.D., 100 cc) each with a flat edge. A hole (1/2" diam.) was drilled in each flat face, a square of separator to be tested placed between the holes, and the cups clamped together. One cup was filled with 40% KOH and the other cup filled with 40% KOH containing 40 ppm zinc ions. Samples of 1 cc were taken at regular intervals and the zinc concentration measured by flame absorption spectroscopy. The samples tested had previously been tested for silver ion diffusion. The results showed that the rate of zincate ion diffusion was of the same order as silver ion diffusion, with a maximum of 4.2 ppm after 150 hours.

3.2.8.8 Effects of aging in 40% KOH with silver present

In order to find out whether long term aging in concentrated caustic in the presence of silver affected the electrical and physical properties of battery separators, the samples of Webril-polysulfone-zirconia separators used to determine silver ion transfer were tested for resistivity and for physical damage. They had been aged for about three months. The resistivity tests were carried out as follows: the first series was run on the samples as they came out of the original KOH solution, and the second series was run after the samples had been vigorously washed in water (in an attempt to remove the black silver or silver oxide precipitate) and then had been re-soaked in KOH before testing.

In 75% of the cases the long term aging in KOH with silver present has no deleterious effect on the specific resistivity of the untreated samples (see Table below). However, the simple act of washing the samples with water resulted in greatly increased specific resistivity values. It is conceivable

that the washing action shook loose the solid particles of the silver or silver oxide precipitate, which then redistributed themselves and obstructed the pores of the separator composite. No obvious correlations could be made between the resistivity values and the different formulations and coating speeds of the samples. No physical changes were observed.

Effect of Long Term Aging in 40% KOH in the Presence
of Precipitated Silver or Silver Oxide

<u>Sample No.</u>	<u>Coating Formulation Ratios by Weight</u>		<u>Specific Resistivity, Ω-in</u>		
	<u>ZrO₂</u>	<u>Polysulfone</u>	<u>Before Ag Test</u>	<u>After Aging</u>	<u>After Aging and Washing</u>
<u>C58-18-1</u> <u>2 ft/min</u>	2	1	30	31	> 1000
<u>C58-18-1</u> <u>3 ft/min</u>	2	1	28	130	> 1000
<u>C58-18-1</u> <u>6 ft/min</u>	2	1	31	49	--
<u>C58-21-2</u> <u>3 ft/min</u>	3	1	65	100	> 1000
<u>C58-24-1</u> <u>2 ft/min</u>	4	1	39	21	310
<u>C58-24-1</u> <u>3 ft/min</u>	4	1	36	11	370
<u>C58-25-1</u> <u>3 ft/min</u>	4	1	31	31	120
<u>C58-27-2</u> <u>5 ft/min</u>	2	1	100	45	500

3.2.8.9 Effects of addition of free zirconia to
sterilization system

The possibility of reducing the weight loss, sustained by battery separator material as a result of sterilization, by introducing free zirconia in the Teflon cells used in the sterilization cycle, was investigated. Fresh samples of runs which had already been tested were sterilized in the presence of 0.01 g of 20-50 mesh zirconia (approximately 10% of the weight of zirconia in the sample). The results in Table XVII indicated that, except in one case, the presence of free zirconia lowered the weight loss induced by the

sterilization step; in three cases the specific resistivity values also declined, and in all cases the resistivity was below the limit imposed by the contract.

This effect was further evaluated by increasing the amount of added zirconia to 0.03 g (approximately 30% of total zirconia present). It was shown that a large amount of free zirconia in the cells further reduces the sterilization weight loss (Table XVIII). The figures in parentheses are the weight losses in the presence of 0.01 g ZrO_2 . Again, except in one case, the resistivity values also decrease as the amount of zirconia in the cell increases. On the basis of these results it seems advisable to add free zirconia, in the amount of between 10 and 30% of the weight of the battery separator composite, to the battery cell in order to reduce both dissolution of zirconia from the separator into the electrolyte and the resistivity of the separator.

3.2.8.10 Effects of pressure on continuously fabricated separators

Throughout the work described in the second phase of this report and especially in the instances where the separators were fabricated continuously in the industrial tower, no particular effort was made to investigate the effect of pressure on the electrical properties of the experimental separators. The reason for this was that, in general, we were able to obtain acceptably low resistivity values without the direct application of pressure. This, of course, simplified the fabricating procedures significantly. On the other hand, the pulling and stretching of the tape during coating, extracting, drying and rolling may actually result in the same effect as that caused by compression.

3.2.9 PREPARATION OF FOOT-WIDE STERILIZABLE SEPARATOR MATERIAL

Having established that the coating mixtures used in most of the experiments yields satisfactory results, the substrate tape remains the variable parameter in the heat sterilizable battery separator system. Kendall's Webril E 1403 (ave. thickness 0.002 inch), which originally gave good support, had deteriorated in quality to a point where it gave nonreproducible results. Webril EM 476 (ave. thickness 0.0027 inch), was claimed to have a fuller structure and to be stronger than E 1403. Pellon tape 2140 was also considered to be promising.

Table XIX indicates some results obtained from tapes whose substrates are Pellon 2140 (3 and 12 inch wide) and Webril EM 476. It can be seen that in the case of the 3 inch Pellon, the weight loss is relatively low and that the sterilization step resulted in a slightly lower thickness. The specific resistivity values of the samples from this run before sterilization were quite high (more than 100 ohms-inch) immediately on testing; however, several hours' soaking in 40% KOH brought these values down to the lower, constant level reported in the table. A trend is shown, where specific resistivity decreases with increasing speed of coating. After the sterilization step, the resistivity values dropped considerably, being well within the limits set by the contract (59 ohms-inch). The rate of electrolyte flow through these samples is low, especially in the case of the 7 foot/min coating; it would indubitably rise if the samples had been soaked in 40% KOH for some time. The conclusions to be drawn from this experiment are that Pellon 2140 coated with our polysulfone:zirconia mixture gives satisfactory results as far as weight loss and resistivity are concerned. The low electrolyte flow rate and high initial resistivity are due to the greater thickness and tighter construction of the uncoated Pellon tape. If the relatively high thickness of the coated tape can be tolerated, this system is to be recommended.

A coating run was made in which the Pellon 2140 used was 12 inch wide. The coating mixture consisted of 1440 g of 20:50 mesh Bio Rad zirconia (well dried), 3680 g of polysulfone:DMAC solution (15% solids) and 19.2 g of Alkaterge E wetting agent. About 210 cc of additional DMAC was used to cut down the viscosity of the suspension. The coating was done at 6 and 5 feet per minute, at an average tower temperature of 72°C. The mix wetted the tape well, and the coated tape was dry and pinhole-free at both speeds. Here again the weight losses were relatively low, and the specific resistivity values were very low after sterilization. Rate of electrolyte flow are good for the sample coated at 6 ft/min, and slow in the case of the 5 ft/min sample. The comments made for the 3 inch wide tape can be applied here.

In the case of Webril EM 476, it was noticed that all the rolls obtained from Kendall were made up of materials which were thinner on one edge than on the other by about 0.3 - 0.4 mil. This non-uniformity often resulted in difficulties during coating in the tower, because the thin edge stretched more than the other, thereby causing creases in the coated tape.

Run C58-74-1 was made using EM 476 and the same coating mixture as that used for the Pellon runs. The tape was coated at 5 and 6 ft/min, at an average tower temperature of 80°C. In general the mix wetted the tape well, and the coated tape was free of pinholes and was smooth; however, longitudinal wrinkles and creases marred the uniformity of the product. The rate of electrolyte flow was relatively fast, most likely related to the lesser thickness and looser construction of the tape. The weight loss after the sterilization test was reasonable, but higher than in the case of Pellon; the initial specific resistivity values were relatively high before sterilization, but decreased to acceptable levels after sterilization.

Another run (C58-75-1) was made using a new EM 476 roll and the same mix as above. Particular pains were taken to improve the alignment of the tower and to avoid wrinkling of the tape. However, stretching of the Webril tape occurred again and resulted in longitudinal wrinkles -- great difficulty was experienced in winding up the coated tape, since the web guide could not be made to work properly because of the lack of opacity of the coated tape. In fact, all the runs made using 12 inch wide material were made difficult by the fact that the coating tower used for this work was originally designed for coating 3 inch - 8 inch wide metal foil; therefore a great deal more labor and care had to be exercised during these runs than would be necessary if there had been the possibility of adjusting the equipment properly.

The coated tape C58-75-1 gave approximately the same results, after sterilization, as those obtained from run C58-74-1; however, the electrolyte flow rate was lower, probably due to the slightly greater thickness of the coated material. In any case, runs C58-75-1 and C58-74-1 demonstrated the feasibility of using Webril EM 476 to good advantage. Most

of the difficulties in obtaining uniform coated tapes were traced to mechanical problems in the coating tower.

Table XX shows the characteristics of five additional coating runs performed on Webril EM 476 and on Pellon 2140. Runs C58-75-2, 76-1, 77-1 and 77-2 used the Webril tape, while run C58-78-1 employed Pellon 2140. In the latter case tests were run only on the section obtained at 5 ft/min; the samples from the other coating speeds (4.5 and 6 ft/min) were not tested because it was decided not to unroll the final roll of coated tape. However, the untested sections looked as good as the section tested.

As frequently mentioned before, the Webril tape causes considerable difficulty in that it easily stretches out of shape while being coated in the tower; its quality is relatively unreproducible and its physical measurements vary from batch to batch. However, it has the advantage that it can be obtained in relatively small thickness (2-3 mils), so that, even when coated, it does not exceed 5 mils in thickness. This low thickness results, on one hand, in more chances for pinholes and flaws, and, on the other hand, in faster electrolyte flow.

Pellon 2140 starts by being thicker and stronger. Coating of this tape has invariably resulted in excellent separator material from the point of view of evenness, homogeneity and lack of pinholes. The electrolyte flow through this material is necessarily slower, especially at the beginning. However, exposure of this material to 40% KOH for a few hours reduces its resistance to the flow of electrolyte very considerably (Fig. 28). Pellon shows, in addition, lesser weight loss than the Webril on sterilization.

As Table XX shows, again the sterilization step brings the specific resistivity values down, well within the limits specified by the contract.

The specific resistivity values before sterilization of the runs shown in this table are consistently higher than those shown in the table. This may have been due to the non-reproducibility of some of the properties of the mix. It was noticed during the runs reported here that the wetting of the tapes by the coating mix was poor and inconsistent, and that, in at least one case (C58-77-1), the coating seemed not to penetrate into the interstices of the tape but to lie over the tape structure. This resulted

in the peeling off of the polymeric coating to give a high weight loss, and also in a lack of small pores through which the electrolyte can flow.

Again, the coated Pellon showed the least weight loss; were it not for its slightly greater thickness and its lesser availability, this material coated with our polysulfone-zirconia mixture would be the preferred combination.

It must also be repeated here that many of the difficulties in coating and rolling the Webril tape are due to mechanical problems existing in the coating tower used here.

The following table lists the significant parameters of the samples sent to JPL for evaluation. All the coated materials are one foot wide, and include only the organic substrate tapes which gave the best results, namely Webril EM 476 and Pellon 2140.

Identification of One Foot-Wide Battery
Separator Material Shipped to JPL

<u>Westinghouse Number</u>	<u>Substrate</u>	<u>Coating Speed, ft/min</u>	<u>Formulation and Procedural Comments</u>
C58-73-1	Pellon 2140	5	The basic coating mixture formulation used consisted of 720 g of 20:50 mesh Bio-Rad, 1840 g of PS:DMAC (13% solids) and 9.6 g Alkaterge E (1%). The oxide:PS ratio was 3:1. The extraction bath consisted of 2 gallons of water and 4 gallons of dioxane.
C58-73-1	"	6	
C58-74-1	Webril EM 476	6	
C58-74-1	"	5	
C58-75-1	"	6	
C58-75-1	"	5	
C58-75-2	"	5.5	
C58-76-1	"	4.5	
C58-76-1	"	5.5	
C58-76-1	"	6	
C58-77-1	"	5	
C58-77-1	"	6	
C58-77-2	"	6.5	
C58-78-1	Pellon 2140	5	
C58-78-1	"	5.75	

4. CONCLUSIONS AND RECOMMENDATIONS

The total research effort of this contract has primarily led to the fabrication of composite membranes able to withstand sterilization conditions. In the second phase of this project the best separator ingredient combination was selected, tested and fabricated, while the first phase led to the development of several instruments and of testing procedures, in addition to the screening and formulation of a number of promising systems.

It is concluded that one foot-wide composite separator membrane can be fabricated by means of a continuous dip-coating process. This type of separator remains dimensionally stable after one sterilization cycle consisting of exposure to 40% KOH at 135°C for 60 hours. In addition, this separator allows only very slow migration of dissolved silver and zinc compounds (less than 35 ppm in 120-150 hours' exposure), while exhibiting specific resistivity values of the order of 40-50 ohms-inch and low resistance to the flow of electrolyte.

Specifically, it is recommended:

1. That the support tape be Webril EM 476 or Pellon 2140. If the former polypropylene tape is used, one can expect fairly uneven void distribution, void size and thickness; this may lead to the generation of pinholes and may be the source of creases and uneven stretching. However, separator composites made using EM 476 will have thicknesses smaller than 6 mils and will exhibit the required low resistivity and relatively high electrolyte flow even before being soaked in 40% KOH.

If the latter tape, Pellon 2140, is used, one will obtain a very strong, entirely coated, pinhole-free composite which is not affected appreciably by the mechanical stresses incurred during the tower coating process. However, generally such separator composites are 7 or 7.5 mils thick and their initial resistivity and resistance to electrolyte flow will be high. This drawback is remedied by presoaking the composite in 40% KOH for a few hours.

2. That the coating mixture consist of polysulfone 1700 (made by Union Carbide Co.), Bio-Rad hydrated zirconia of 20-50 mesh, and dimethylacetamide accompanied by a wetting agent (Alkaterge E). The ingredient composition recommended is as follows: oxide:polysulfone ratio should range between 2 and 4, with 3 being the most promising; the polysulfone:dimethyl acetamide ratio is 15:100 by weight and the amount of wetting agent is 1% by weight of solids. An example of a typical formulation is: 720 g of vacuum oven dried 20:50 mesh Bio Rad zirconia, 1840 g of polysulfone:dimethylacetamide solution (15:100), 9.6 g of Alkaterge E.

This mix should be ball milled for at least 3 days. This amount of material is sufficient to coat between 50 and 100 feet of one foot wide tape, depending on the volume of the dip-coating tank and on other procedural parameters.

3. That the method for applying the mixture to the tape be a dip-coating procedure. Care must be taken to stir the mixture thoroughly to keep the oxide in suspension; however, generation of air bubbles must be avoided. Spreader bars may be used for making the mixture penetrate into the interstices of the web and for removing excess mix.

4. That the method for removing the solvent dimethylacetamide and coagulating the polysulfone, at the same time causing pores to form in the composite, be that of dipping the coated tape into an agitated extraction-coagulation bath consisting of 1 part water:2 parts dioxane (6 gallons/100 feet).

5. That coating speeds range from 5 to 7 feet per minute with a heating tower temperature of no more than 80°C. Higher temperatures make the coated tapes shrink and/or curl; in addition, especially in the case of the Webril, there might be a chance of the tape melting.

6. That more work be done with the aim of improving the reproducibility of the properties of the sterilizable separators of this project, mainly by the use of more homogeneous, thinner and novel polypropylene substrates.

Table I

Sterilization of Polymeric Candidates

Weight and Dimension Changes of Polymer Sheet Exposed for 60 Hours
to Aqueous 40% KOH at Room Temperature (RT) or 135°C

<u>Sample</u>	<u>% weight change</u>		<u>Dimension change (%)</u> <u>after heating at 135°C</u>	
	<u>RT</u>	<u>135°C</u>	<u>av. lgth. and width</u>	<u>thickness</u>
<u>Resistant Materials</u>				
Polypropylene Pellon OP698	-0.52	-6.1	-3	0
Webril Polypropylene support mat, Kendall	-2.5	-3.2	-3	0
Dupont 100X Teflon	+0.1	-0.3	<1	0
Aico Teflon Felt	-1.1	-1.4	<1	-5
G.E. Polyphenylene Oxide	-0.6	-4.7	<1	0
Cast Epoxy Shell 826, Metaphenylenediamine hardener	-0.04	+1.6	0	0
Nordel-Ethylene propylene- Terpolymer Dupont	-0.64	-1.3	-1	-1
Asbestos Teflon Knowlton Bro.	-2.4	-2.0	-3	-20
Polysulfone Union Carbide	-	+0.1	-	0

(Continued)

Table I (continued)

<u>Sample</u>	<u>% weight change</u>		<u>Dimension change (%)</u> <u>after heating at 135°C</u>	
	<u>RT</u>	<u>135°C</u>	<u>av. lgth. and width</u>	<u>thickness</u>
<u>Less Resistant Materials</u>				
Fluorocarbon Paper (AMF)	-13.2	-17.7	-1	-19
Viscose Rayon Cotton Pulp Impreg. with Phenolic Resin FMC	-12.6	-41.2	+31	-15
Battery Paper, Hemp Crane	-15.6	-38.6	-19	-12
Viton-Copolymer vinylidene fluoride and hexafluoropropylene, Dupont	-0.12	dissolved	---	---
Microporous Rubber American Hard Rubber	-21.9	-29.2	-2	-4
Crane Asbestos Paper	-13.8	-28.1	+16	-33
Dow Badische Saran Cloth	+1.0	-60.4	-32	+33
Dow Badische Acrylic Cloth	-0.7	dissolved	---	---
Chemstrand Acrilan	+0.9	dissolved	---	---
Crane Orlon Paper	-4.0	dissolved	---	---
Acrylic Fiber Paper (Am. Cyanamid)	-1.2	-60.7	-16	+50
Nomex Paper Polyamide	+0.25	dissolved	---	---
Dexter Battery Sheet	-22.3	-4.43	-0.2	-20

Table II

Solubility of Inorganic Filler Materials

	Solubility in 40% KOH at 25°C (grams/100 ml)
1. Zirconium phosphate	1.99
2. Zirconium tungstate	3.58
3. Zirconium molybdate	3.04
4. Zirconium oxide (hydrous)	.06
5. Molecular Sieve 4A	.11
6. Molecular Sieve 5A	.13
7. Molecular Sieve 13A	.31
8. Calcium zirconate	.20
9. Strontium zirconate	.00
10. Barium zirconate	.00
11. Magnesium zirconate	.18
12. Zinc zirconate	1.61
13. Calcium stannate	.09
14. Strontium stannate	.07
15. Barium stannate	.28
16. Zinc stannate	3.82
17. Titanium oxide	gain 4% weight
18. Stannous oxide	2.10
19. Stannic oxide	.08
20. Silicic acid	over 4.0
21. Neutral alumina	.43
22. Ammonium molybdenum phosphate	over 4.0
23. Asbestos (acid washed)	1.9
24. Aluminum silicate	.37
25. Calcium tungstate	2.89
26. Tungstic acid	over 4.0
27. Thorium oxide	.08
28. Barium arsenate	1.07
29. Zinc silicate	over 4.0
30. Copper ferrocyanide	2.74
31. Magnesium oxide	gain 100% weight
32. Magnesium stannate	.09

Table III

Battery Separator Compositions

Number	Thickness (mils)	Single Sheet-SS or Sandwich-SW	Polymer Binder	Solvent for Binder	Filler	Drying Conditions	Weight (grams)	
							Uncoated	Coated
55-7-20-4	3.8	SS	Kynar	DMAC ^(a)	Zr(OH) ₄	Air-dried, Room Temp (RT)		
56-7-21-1	3.9	SS	Polyphenylene Oxide	Toluene	Zr(OH) ₄	10 min, 100°C		
56-7-21-2	2.0	SS	Polyphenylene Oxide	Toluene	None	Air-dried, RT		
56-7-21-3	4.6	SS	Polyphenylene Oxide	Toluene	Zr(OH) ₄	Air-dried, RT		
57-7-22-1	3.3	SS	Polyphenylene Oxide	Toluene	Zr(OH) ₄	Air-dried, RT		
57-7-22-2	3.5	SS	Polyphenylene Oxide	Toluene	Zr(OH) ₄ ^(b)	10 min, 100°C		
57-7-22-3	2.2	SS	Polysulfone	o-Dichlorobenzene	None	10 min, 100°C	0.21	0.29
57-7-22-4	1.8	SS	Kynar	DMAC	None	RT, 15 min. at 0.5 Torr	0.22	0.25
58-7-22-1	3.2	SW	Kynar	DMAC	None	RT, 15 min. at 0.5 Torr	0.42	0.51
60-7-25-1	3.1	SS	Kynar	DMAC	Zr(OH) ₄ ^(b)	15 min, 100°C	0.22	0.40
60-7-25-2	5.4	SW	Kynar	DMAC	Zr(OH) ₄	15 min, 100°C	0.44	0.66
62-7-26-1	1.8	SS	Phenoxy Resin (Poron)	DMAC	None	15 min, 100°C	0.22	0.24
62-7-26-2	3.0	SS	Phenoxy Resin (Poron)	DMAC	Zr(OH) ₄ ^(b)	15 min, 100°C	0.21	0.34

(Continued)

(a) Dimethylacetamide.

(b) Ballmilled in water, other Zr(OH)₄ used as received.

Table III(continued)

Number	Thickness (mils)	Single Sheet-SS or Sandwich-SW	Polymer Binder	Solvent for Binder	Filler	Drying Conditions	Weight (grams)	
							Uncoated	Coated
32-8-10-1	2.6	SS	Polysulfone	o-Dichlorobenzene	MgO	30 min, 100°C	0.20	0.32
33-8-11-1	3.1	SS	Poron	DMAC	MgO	30 min, 100°C	0.20	0.28
37-8-25-2	7.1	SW	Poron	DMAC	Zr(OH) ₄	30 min, 100°C	0.39	1.16
40-9-1-1	2.8	SS	Kynar	DMAC	Zr(OH) ₄	30 min, 100°C	0.18	0.28
41-9-1-1	4.9	SW	Kynar	DMAC	Zr(OH) ₄	30 min, 100°C	0.37	0.89
41-9-1-2	2.5	SS	Poron	DMAC	Zr(OH) ₄	30 min, 100°C	0.19	0.51
42-9-1-1	11.7	SW	Poron	DMAC	Zr(OH) ₄	30 min, 100°C	0.39	2.47
42-9-2-1	4.5	SS	Polysulfone	o-Dichlorobenzene	Zr(OH) ₄	30 min, 100°C	0.20	0.60
43-9-2-1	8.0	SW	Polysulfone	o-Dichlorobenzene	Zr(OH) ₄	30 min, 100°C	0.40	1.42
43-9-2-2	3.7	SS	Polysulfone	DMAC	Zr(OH) ₄	30 min, 100°C	0.20	0.48
44-9-2-1	9.5	SW	Polysulfone	DMAC	Zr(OH) ₄	30 min, 100°C	0.38	1.38
44-9-6-1	4.8	SS	Polysulfone	DMAC	CaO	30 min, 100°C	0.19	0.76
45-9-7-1	2.2	SS	Polysulfone	DMAC	CaO	30 min, 100°C	0.19	0.32
46-9-7-1	4.0	SS	Polysulfone	DMAC	CaO	30 min, 100°C	0.20	0.87
47-9-9-1	1.7	SS	Polysulfone	N,N Dimethyl Formamide	--	30 min, 100°C	0.20	0.26
47-9-9-2	4.4	SS	Polysulfone	N,N Dimethyl Formamide	Zr(OH) ₄	30 min, 100°C	0.20	0.66
48-9-9-1	11.1	SW	Polysulfone	N,N Dimethyl Formamide	Zr(OH) ₄	30 min, 100°C	0.38	1.66
48-9-9-2	3.0	SS	Polysulfone	N,N Dimethyl Formamide	Zr(OH) ₄	30 min, air dry - RT 45 min, 100°C	0.20	0.54

Table III (continued)

Number	Thickness (mils)	Single Sheet-SS or Sandwich-SW	Polymer Binder	Solvent for Binder	Filler	Drying Conditions	Weight (grams)	
							Uncoated	Coated
62-7-26-3	4.5	SW	Phenoxy Resin (Poron)	DMAC	Zr(OH) ₄ ^(b)	15 min, 100°C	0.42	0.57
24-8-8-1	2.3	SS	Polysulfone	DMAC	--	30 min, 100°C	0.19	0.29
25-8-8-1	5.0	SS	Polysulfone	DMAC	MgO	30 min, 100°C	0.19	0.55
25-8-8-2	3.1	SS	Polysulfone	DMAC	MgO	30 min, 100°C	0.18	0.35
26-8-8-1	2.7	SS	Polysulfone	DMAC	MgO	30 min, 100°C	0.19	0.33
27-8-9-1	3.2	SS	Polysulfone	DMAC	MgO	30 min, 100°C	0.19	0.30
27-8-9-2	1.9	SS	Poron	DMAC	--	90 min, 100°C	0.19	0.23
27-8-9-3	2.1	SS	Poron	DMAC	--	30 min, 100°C	0.20	0.23
28-8-9-1	4.1	SS	Poron	DMAC	MgO	30 min, 100°C	0.21	0.53
28-8-10-1	4.8	SS	Poron	DMAC	MgO	30 min, 100°C	0.20	0.56
28-8-10-2	2.6	SS	Poron	DMAC	MgO	30 min, 100°C	0.18	0.35
29-8-10-1	1.6	SS	Kynar	DMAC	--	30 min, 100°C	0.19	0.23
29-8-10-2	4.0	SS	Kynar	DMAC	MgO	30 min, 100°C	0.20	0.40
30-8-10-1	3.6	SS	Kynar	DMAC	MgO	30 min, 100°C	0.19	0.34
30-8-10-2	2.2	SS	Kynar	DMAC	MgO	30 min, 100°C	0.18	0.24
30-8-10-3	1.5	SS	Polysulfone	o-Dichlorobenzene	--	30 min, 100°C	0.18	0.20
31-8-10-1	3.0	SS	Polysulfone	o-Dichlorobenzene	MgO	30 min, 100°C	0.19	0.35
31-8-10-2	2.0	SS	Polysulfone	o-Dichlorobenzene	MgO	30 min, 100°C	0.18	0.27

(Continued)

Table IV

Electrical Characteristics of Experimental Membranes
 (Filler makes up the major portion of the polymer-filler wgt.)

Support/Binder	Filler	Thickness mils	% Polymer + Filler by wgt.	Electrical Resistivity (ohm-cm)	Remarks
Webril/Polysulfone	None	2.2	13	727.7	--
"	ZrO	3.7	60	140.4	--
"	ZrO	5.6	27	218.6	--
Webril/Polysulfone	TiO ₂	2.0	42	565.4	--
"	TiO ₂	3.8	33	143.1	--
"	TiO ₂	5.1	63	350.3	--
Webril/Polysulfone	TiO ₂	3.8	34	52.0	--
"	TiO ₂	3.1	14	311.0	--
"	TiO ₂	3.2	4.5	127.3	--
3 sheets Webril/Polysulfone	CaO	6.2	54	58.0	--
2 sheets "	CaO	5.5	70	130.5	--
1 sheet "	CaO	2.8	66	57.3	--

(Continued)

Table IV (Continued)

Support/Binder	Filler	Thickness mils	% Polymer + Filler by wgt.	Electrical Resistivity (ohm-cm)	Remarks
Webril/Phenoxy	ZrO	5.4	23	319.7	Oven baked
"	ZrO	5.5	31	438.3	"
"	ZrO	4.0	50	230.4	"
Webril/Polysulfone	Polyethylene Oxide (Extracted)	4.7	26	104.8	
Webril/Polysulfone	Linde 5A	7.5	--	34.2	All samples approximately 50% by wgt. (Filler + polymer)
"	Linde 4A	7.0	--	53.1	
"	Linde 3A	6.1	--	72.2	
"	Linde 13X	6.6	--	60.9	
"	Zeolon	5.9	--	30.4	

TABLE V

Effects of Extraction by Water-DMAC Solutions

Time of Extraction (min)	How Dried	Unpressed Wet Thickness (mils)	Unpressed Resistance (ohms)	Pressed* Wet Thickness (mils)	Pressed* Resistance (ohms)
1	air	3.7	1.78	3.5	.65
1	oven	3.8	over 100	3.6	1.60
10	air	3.6	22.4	35	1.08
10	oven	4.3	over 100	315	4.57
1000	air	3.6	53.9	2.8	1.82
1000	oven	3.2	71.0	2.8	8.96

*Pressed with 5000 lb load on ram.

Table VI

Weight Changes of Water-Precipitated Membranes on Sterilization Cycling

Material	Conditions	% Weight Change
Polysulfone, 15 g/100 ml DMAC	Cycled 60 hr-40% KOH- 135°C. Dried, 1 hr. 110°C.	-1.3
"	"	-2.5
"	"	-1.1
"	"	-1.4
Polysulfone, 15 g/100 ml DMAC + 5 g titanic oxide	"	-21.6
Polysulfone, 15 g/100 ml DMAC + 5 g Zeolon H	"	-25.0
Polysulfone, 15 g/100 ml DMAC + 5 g Zr(OH) ₄	"	-21.5
" (Duplicate)	"	-21.9
Polysulfone, 15 g/100 ml DMAC + 5 g Linde 10X molecular sieve	"	-24.9
" (Duplicate)	"	-24.6

Table VII

Filler Residue after Sterilization Cycling

Cycled and uncycled Water Precipitated Membranes Fired 2 hr, 660°C

	Material	Conditions	% Weight Material Remaining
	Polysulfone, 15 g/100 ml DMAC, 5 g Zr(OH) ₄	Sample air dried for 1 hr. at 110°C. Weighed, then fired.	18.2
	" Duplicate	"	20.5
<u>Cycled</u>	Polysulfone, 15 g/100 ml DMAC, 5 g Zr(OH) ₄	" Cycled weight compared to fired weight	4.3
<u>Cycled</u>	" Duplicate	"	1.2
	Polysulfone, 15 g/100 ml DMAC, 5 g Linde molecular sieve	" Sample air dried 1 hr, 110°C. Weighed, then fired.	23.8
	" Duplicate	"	20.0
<u>Cycled</u>	Polysulfone, 15 g/100 ml DMAC, 5 g Linde molecular sieve	" Sample air dried 110°C. Weighed, then fired-cycled weight compared to fired weight.	0.5
<u>Cycled</u>	" Duplicate	"	1.0
	Polysulfone, 15 g/100 ml DMAC, no filler	" Sample air dried 1 hr. 110°C. Weighed, then fired.	<0.05
	" Duplicate	"	<0.05
	Polysulfone, 15 g/100 ml DMAC, no filler	Cast in water (1 hr). Air dried 1 hr, 110°C, 1 hr. Then fired to	0.41
	Ball milled for 16 hours	meas. ball mill pickup.	0.42
	"	"	0.46

TABLE VIII

Effects of Excess Filler on Filler Residue After Sterilization

Test No.	Filler Loading (g filler/ 15 g polysulfone)	Cycled without excess filler	Cycled with 2 g excess filler	Wgt. % change
1	5 Zr(OH) ₄	2 cycles	--	-25.6
2	15 Zr(OH) ₄	--	1 cycle	-3.5
3	5 Zr(OH) ₄	--	1 cycle + 2 g Ag ₂ O	+27.4 (+ 22% Ag)
4	10 Zr(OH) ₄	--	1 cycle + 2 g Ag ₂ O	+0.4 (+ 4% Ag)
5	20 Zr(OH) ₄	--	1 cycle + 2 g Ag ₂ O	-2.2 (+ 4% Ag)
6	5 Zeolon H	1 cycle	--	-25
7	5 Zeolon H	--	1 cycle 1 cycle 1 cycle	-19.4 -19.5 -18.6
8	5 Linds, 10 X	1 cycle 2 cycles	-- --	-24.9 -27.4

(Continued)

TABLE VIII (Continued)

Test No.	Filler Loading (g filler/ 15 g polysulfone)	Cycled without excess filler	Cycled with 2 g excess filler	Wgt. % change
9	5 Linde 10 X	--	1 cycle	-13.8
			1 cycle	-13.8
			1 cycle	-13.8
10	5 Linde 3 A	1 cycle	--	-23.2
		Fired % remaining 0.4%		-22.8
		0.5%		-22.5
11	5 Linde 3 A	--	1 cycle	-19.2
			1 cycle	-18.7
			1 cycle	-18.8
12	5 Linde 13 X	1 cycle	--	-25.6
			Fired % remaining 0.1%	-26.0
			1.2%	-24.2
13	5 Linde 13 X	--	1 cycle	-19.1
			1 cycle	-18.4
			1 cycle	-17.0
14	5 Titanium oxide	1 cycle	--	-21.6
15	5 Titanium oxide	--	1 cycle	+ 6.1
			1 cycle	+ 6.1
			1 cycle	+ 6.8

* Each cycle 60 hr at 135°C in 40% KOH.

TABLE IX

Membrane Tensile Strength

Cast Unsupported Polymer Film

10 g Zr(OH)₄/15 g Polysulfone/100 ml DMAC (40% filler)

Film Thickness 2.1-2.2 mils

Wet strength PSI		Dry strength PSI	
550		405	
527		317	
529		399	
441	<u>Average 511 PSI</u>	413	<u>Average 397 PSI</u>
504	<u>Av. Elongation 12%</u>	453	<u>Av. Elongation 6%</u>

Film Thickness 4.2-4.5 mils

Wet strength PSI		Dry strength PSI	
433		446	
462		441	
470		513	
443		464	
462	<u>Average 454 PSI</u>	436	<u>Average 460 PSI</u>
	<u>Av. Elongation 16%</u>		<u>Av. Elongation 11%</u>

TABLE IX cont.

Membrane Tensile Strength

Unsupported Film, 26% by wgt. $Zr(OH)_4$ in Polysulfone

Film Thickness 3.0 mil

As cast strength PSI		Cycled strength PSI	
482		417	
468		433	
513		333	
474		414	
538	<u>Average 502 PSI</u>	432	<u>Average 406 PSI</u>
537	<u>Av. Elongation 10%</u>		<u>Av. Elongation 3%</u>

19% loss in tensile strength, one cycle

70% loss in elongation, one cycle

Coated 3 mil Webril Polypropylene, 26% by wgt. $Zr(OH)_4$ in Polysulfone

Coated Thickness 4.9-5.2 mil

As coated strength PSI		Cycled strength PSI	
6080		3490	
5830		4450	
5810		4290	
5600		4200	
6550		4770	
5580	<u>Average 5908 PSI</u>	3950	<u>Average 4192 PSI</u>
	<u>Av. Elongation 3 1/2%</u>		<u>Av. Elongation 26%</u>

29% loss in tensile strength, one cycle

24% loss in elongation, one cycle

TABLE IX cont.

Membrane Tensile Strength

As Cast vs. Cycled Condition


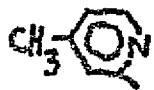
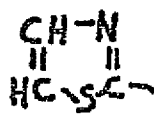


Coated 3 mil Webril Polypropylene, 6% Zr(OH)₄ by wgt. in Polysulfone

<u>As coated strength PSI</u>	<u>Cycled strength PSI</u>
5340	3450
4590	4160
6850	4170
4750	4190
6790	4010
6440	3380
<u>Average 5793 PSI</u>	<u>Average 3893 PSI</u>
<u>Av. Elongation 38%</u>	<u>Av. Elongation 25%</u>

33% loss in tensile strength, one cycle







34% loss in elongation, one cycle

Table X

Cmpd. No.	8-Hydroxyquinoline derivatives of structure I					
	<u>R₁</u>	<u>R₂</u>	<u>Reaction time (days)</u>	<u>Yield (%)</u>		<u>Solvent system for recrystallization^a</u>
				<u>crude</u>	<u>recryst.</u>	
1		phenyl	22	26	22	(A) 50 ml dimethylformamide (B) 100 ml ethanol + 150 ml H ₂ O
2		phenyl	28	72	40	(A) 100 ml pyridine (B) 300 ml acetone
3		phenyl	28	34	29	(A) 150 ml pyridine (B) 300 ml acetone
4		phenyl	27	11	--	---
5		phenyl	29	71	50	(A) 100 ml pyridine (B) 300 ml absolute ethanol
6	phenyl	phenyl	43	8	7	(A) 75 ml acetone (B) 100 ml ethanol + 100 ml water

(Continued)

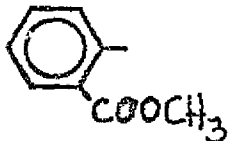
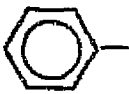
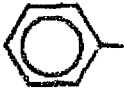
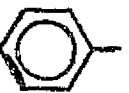
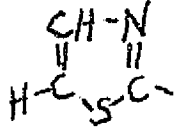
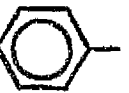
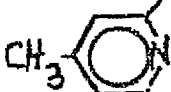



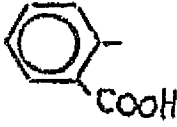
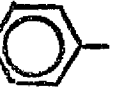

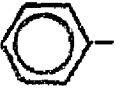
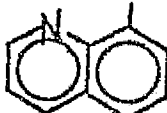
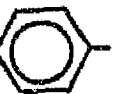
Table X (continued)

<u>Compd. No.</u>	<u>R₁</u>	<u>R₂</u>	<u>Reaction time (days)</u>	<u>Yield (%)</u>		<u>Solvent system for recrystallization^a</u>
				<u>crude</u>	<u>recryst.</u>	
7		phenyl	31	40	--	---
8		phenyl	38	36	21	(A) 50 ml pyridine (B) 100 ml absolute ethanol
9		CH ₃ -CH ₂ -CH ₂ -	40	31	--	---
10		phenyl	31	50	42	(A) 30 ml acetone (B) 130 ml 95% ethanol
11			11	80	70	(A) 500 ml acetone (B) 400 ml ethanol

a. The recrystallization procedure involved dissolving in hot (A), filtering hot, adding (B) and cooling.

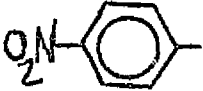
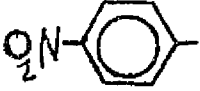
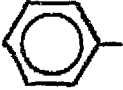
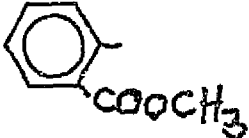


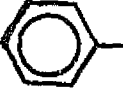
Table XI

Epoxy Resins Containing 8-Hydroxyquinoline Groupings^a

8-Hydroxyquinoline precursor		Wt. used (grams)	% wt. change after exposure to KOH solution at 135°C
<u>R₁</u>	<u>R₂</u>		
		0.96 0.48	1.8 0.64
		0.82 0.40	0.23 0.68
		0.83 ^c 0.41	12.8 5.2
		0.85 0.43	0.60 1.5
		0.96 0.48	6.3 3.3
		0.93 0.46	b 6.6
		0.82 0.41	-0.13 0.48
		0.94 0.47	0.48 0.23

(Continued)

Table XI(Continued)

8-Hydroxyquinoline precursor		Wt. used (grams)	% wt. change after exposure to KOH solution at 135°C
<u>R₁</u>	<u>R₂</u>		
	CH ₃ CH ₂ CH ₂ -	0.84 0.42	-40.4, -24.1 ^b -0.34
		0.93 0.46	0.26 0.64
		0.96 0.38	-5.7 2.8
		0.86 0.43	2.3 0.83

-
- a. Resins were prepared from 0.92 grams Shell Epon 826 and 0.134 grams m-phenylenediamine. Curing conditions were 6 hours at 140°C, except as noted.
- b. The product from this reaction mixture did not give a coherent resin. It was not tested further.
- c. Curing temperature 150°C.

Table XII

Interaction of epoxy resins derived from oxine derivatives
with copper acetate or with NaOH

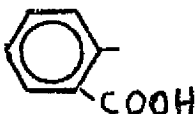
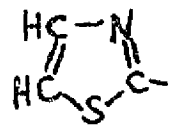

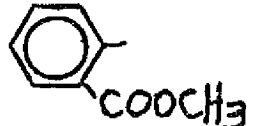
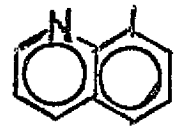
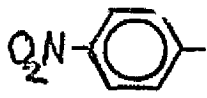


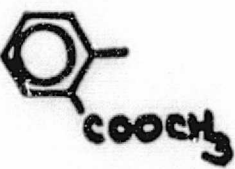



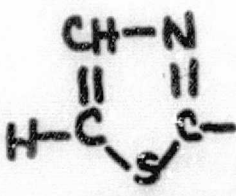



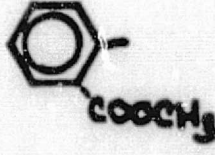

8-Hydroxyquinoline precursor		<u>Tested with copper acetate</u>	<u>Moles OH⁻ consumed per mole of oxine precursor</u>
<u>R₁</u>	<u>R₂</u>		
	phenyl	yes	0.35
	phenyl	no	0.13
	phenyl	yes	0.16
	phenyl	yes	0.15
phenyl	phenyl	yes	not tested
	phenyl	yes	not tested
	phenyl	yes	not tested

TABLE XIII







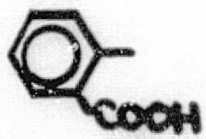

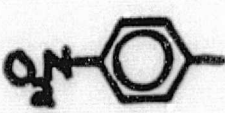
Electrical Resistivities of Polysulfone Films Containing
Chelating Epoxy Resins as Fillers

R_1	R_2	Applied Pressure (lbs/in ²)	Average* Resistivity (ohm-cm)
		0	high
		200	281
		5000	2.9
		0	801
		200	63.1
		5000	55.7
		0	1157
		200	179
		5000	147
		10000	140
		0	528
		200	47.0
		5000	40.7
		0	1102
		200	34.6
		5000	33.5
		0	high
		200	92.6
		5000	95.9

*Average of five values

(Continued)

TABLE XIII(Continued)

R_1	R_2	Applied Pressure (lbs/in ²)	Average* Resistivity (ohm-cm)
		0	1570
		200	54.5
		5000	49.3
		0	high
		200	38.2
		0	high
		200	68.6
		5000	54.7
		0	high
		200	43.9
		5000	38.9
	C_9H_7	0	510
		200	43.8
		5000	32.3

*Average of five values

TABLE XIV

Identification of Samples for Resistance to Sterilization Tests

Sample No.	Polysulfone	Oxide: PS ratio	Coating Speeds, ft/min.	Comments
C58-18-1	PS 1700	2:1	2, 3, 6	Ball milled 9 days
C58-21-2	PS 1700	3:1	3	Ball milled 10 hours
C58-24-1	PS 1700	4:1	2,3	Ball milled 24 hours
C58-25-1	PS 1700	4:1	3	Ball milled 8 days
C58-27-2	PS 1700	2:1	5	Ball milled 57 days
C58-29-1	P 361	3:1	2, 4, 6	Ball milled 7 days, New Webril
C58-31-1	P 361	3:1	3, 5	Ball milled 67 hours, New Webril
C58-31-3	P 361	2:1	2, 3, 6	Ball milled 27 hours, New Webril

TABLE XV (cont)

Sterilization cycle: 60 hours at 135°C in 40% KOH

Sample No.	Coating speed, ft/min.	Thickness before sterilization, mils		Thickness after sterilization, mils		Weight change after Sterilization, %	Specific resistivity before sterilization, ohm - cm	Specific resistivity after sterilization, ohm-cm	Comments
C58-29-1	2	2.2	2.2	1.75	1.8	-33	68	85	Both KOH solution and sample are yellow. Sample resembles plain Webril. Coating is no
		2.5	2.1	2.0	2.0				
C58-29-1	4	2.2	2.35	1.75	2.3	-43	46	108	
		2.6	3.3	1.8	2.25				
C58-29-1	6	3.2	3.0	1.9	1.9	-51	18	130	
		3.2	3.25	1.8	1.85				
C58-31-1	3	3.8	3.6	2.0	1.9	-65	31	--	
		4.15	3.9	1.8	1.6				
C58-31-1	5	3.0	3.4	2.0	1.9	-54	38	66	
		3.05	2.7	2.05	1.6				
C58-31-3	2	3.5	3.3	2.35	2.0	-58	37 (700)	130	
		3.3	3.1	1.9	2.1				
C58-31-3	3	2.35	2.35	2.0	2.2	-38	290	120	
		2.5	2.55	1.8	1.75				
C58-31-3	6	2.75	2.7	1.9	1.95	-58	260	130	
		3.0	3.05	2.4	1.80				
Plain Webril	-	1.7	1.9	2.0	1.9	-1.7	--	--	KOH solution is slightly yellow. Sample unchanged except for curling at edges.
		1.8	1.65	1.8	2.0				

TABLE XV

Effects of Sterilization Cycling on Thickness, Resistivity and Weight
Sterilization cycle: 60 hours at 135°C in 40% KOH

Sample No.	Coating speed, ft/min.	Thickness before sterilization, mils		Thickness after sterilization, mils		Weight change after Sterilization, %	Specific resistivity before sterilization, ohm-cm	Specific resistivity after sterilization, ohm-cm	Comments
C58-18-1	2	3.2	3.4	3.3	3.4	-8.5	75	59	No change in physical characteristics of separator and of KOH solution.
		3.5	4.9	3.65	4.6				
C58-18-1	3	3.7	3.55	3.4	3.65	-7.4	73	59	
		4.45	4.42	3.5	5.2				
C58-18-1	6	5.5	3.95	4.6	3.7	-8.7	73	34	
		3.40	3.45	3.55	3.0				
C58-21-2	3	3.9	4.0	4.0	4.2	-7.4	83	--	
		3.65	4.05	3.3	3.95				
C58-24-1	2	4.0	4.0	3.9	3.2	-9.0	106	--	
		3.6	4.4	3.65	2.9				
C58-24-1	3	4.7	4.8	3.7	4.0	-8.7	96	--	
		3.45	3.3	3.3	2.8				
C58-25-1	3	4.55	3.8	4.35	3.85	-9.6	785	--	A crease in separator appeared, likely caused by pressure from cell cover. Some flaking at crease.
		4.05	3.8	4.1	3.7				
C58-27-2	5	2.0	2.0	1.95	1.9	-16.2	240	400	No change in separator. KOH solution slightly yellow
		2.0	1.95	1.8	2.0				

TABLE XVI

Effects of Oxide and Wetting Agent Concentrations on Thickness, Weight and Resistivity after Sterilization

Sample No.	ft/min	Thickness Before Sterilization in Mils		Sample Appearance (Color, physical, mechanical properties and size)	Thickness After Sterilization in Mils		Percent Wt. Change	Specific Resistivity Before Sterilization Ω -in	Specific Resistivity After Sterilization Ω -in
C58-43-1 Beginning	2	1.9	2.0	Unchanged	2.0	1.9	-12	> 200	42
		2.18	2.1		2.1	2.0			
C58-43-1 End	2	2.4	2.2	Unchanged	2.1	2.25	-9.5	> 200	55
		2.4	2.1		2.4	2.1			
C58-43-1 Beginning	3	2.1	2.35	Unchanged	2.1	2.15	-10.3	> 200	122
		2.05	2.3		2.4	2.5			
C58-43-1 End	3	2.1	2.05	Unchanged	1.95	1.9	-11.2	> 200	135
		1.9	2.1		2.15	1.7			
C58-43-1 Beginning	4	2.1	2.3	Unchanged	2.25	2.0	-12.1	> 200	60
		2.2	2.18		2.0	2.3			
C58-43-1 End	4	2.18	2.15	Unchanged	2.1	2.4	-10.4	> 200	51
		2.2	2.2		2.15	2.0			
C58-43-1 Beginning	5	2.15	2.6	KOH clear, sample slightly yellow	2.6	2.4	-8.6	> 200	40
		1.9	2.2		2.0	2.55			
C58-43-1 End	5	2.15	2.05	KOH clear, sample slightly yellow	2.15	2.3	-27.5	> 200	30
		2.2	2.2		2.15	2.1			
C58-44-1 Beginning	4.5	2.85	3.05	Unchanged	3.15	2.4	-10%	> 170	120
		2.6	2.6		2.4	2.8			
			3.0		2.4	2.5			

TABLE XVI (cont)

Sample No.	ft/min	Thickness Before Sterilization in Mils		Sample Appearance (Color, physical, mechanical properties and size)	Thickness After Sterilization in Mils		Percent Wt. change	Specific Resistivity Before Sterilization Ω -in	Specific Resistivity After Sterilization Ω -in
C58-44-1 End	4.5	3.0 2.5	2.9 3.2 2.6	Unchanged	2.9 2.4	2.7 3.3 2.4	-9.6	>170	130
C58-44-1 Beginning	5	2.9 3.0	3.0 2.85 3.0	Unchanged	2.5 2.9	2.75 2.65 2.7	-9.3	>170	85
C58-44-1 End	5	2.7 2.6	2.9 3.0 2.9	Unchanged	2.65 2.9	3.0 2.55 2.75	-10.4	>170	45
C58-44-1 End	5.5	2.85 3.0	2.7 2.75 2.6	Unchanged	2.9 2.4	3.0 2.5 2.5	-8.0	>170	>170
Plain Webril EM-476	--	3.3 3.0	2.9 3.1 3.2	KOH and sample both green/ yellow color (badly curled)	3.75 3.8	3.4 4.0 3.1	-0.49	0	0
Plain Webril H-751	--	4.4 4.9	4.9 4.6 4.4	KOH clear, sample slightly yellow color (badly curled)	6.9 7.4	7.1 7.5 7.4	-0.6		300
Plain Webril E1451	--	5.6 5.6	5.5 6.2 5.5	KOH clear, sample yellow/ green color	5.7 6.5	5.9 6.8 6.4	-0.71	----	7
Plain Webril E1452	--	5.9 5.7	5.4 5.9 5.9	KOH clear, sample yellow/ green color	6.2 6.3	6.2 7.4 5.8	-1.0	----	35
Plain Webril H739	--	5.1 5.3	6.0 5.2 5.1	KOH clear, sample curled - sample yellow/green color	9.4 8.3	6.9 9.0 9.0	-1.4	----	35

TABLE XVI (cont)

Sample No.	ft./min. and Temp.	Thickness Before Sterilization in Mils		Sample Appearance (Color, Physical, Mechanical, Properties and Size After Sterilization)	Thickness After Sterilization in Mils		Percent Wt. Change	Specific Resistivity Before Sterilization Ω -inch	Specific Resistivity After Sterilization Ω -inch
C58-53-2	3	4.6	4.4	No change	3.8	3.85	-13.3%	50	41
	(71°C)	4.2	4.15		4.0	4.05			
C58-53-2	3.5	5.0	4.6	No change	3.6	3.95	-18.4%	50	39
	(71°C)	4.4	4.5		4.7	4.45			
C58-53-2	4	4.8	4.6	KOH Light Green No change in Sample	3.65	3.65	-12.0	73	85
	(70°C)	4.0	4.3		4.4	4.2			
C58-53-2	4	4.25	4.35	No change	3.75	3.65	-12.9	58	14
	(71°C)	4.25	4.7		4.55	4.5			
C58-56-1 "A"	3	3.4	4.0	No change	3.15	3.1	-14.4%	97	24
	(71°C)	3.25	3.5		3.0	3.4			
C58-57-1	3.5	5.3	5.2	No change	3.75	4.3	-11.8	254	92
	(70°C)	5.2	4.7		4.7	4.15			
C58-58-1	3.5	3.5	3.45	No change	3.2	2.9	-13.3	160	60
	(78°C)	3.4	3.3		3.1	3.5			

TABLE XVII

STERILIZATION PROGRAM (135°C FOR 60 HOURS IN 40% KOH)
 Effect of Excess Zirconia (10%) on Sterilized Membranes

Sample No.	ft/min	Thickness Before Sterilization in Mils		Sample Appearance (Color, physical, mechanical properties and size)	Thickness After Sterilization in Mils		Percent Wt. Change	Previous % Wt. Change	Specific Resistivity Before Sterilization Ω -in	Specific Resistivity After Sterilization Ω -in
C58-53-2 (71°C)	3	4.2	4.5	No Change	3.75	3.85	-10.9	-13.3	50	37
		4.6	4.5 5.0		4.7	4.2 4.4				
C58-53-2 (71°C)	3.5	4.7	4.25	No Change	4.15	3.4	-12.8	-18.4	50	36
		4.5	4.6 4.6		4.15	4.8 4.2				
C58-53-2 (70°C)	4	3.8	4.15	No Change	3.5	3.2	-15.6	-12	73	125
		4.8	4.5 4.8		4.3	4.15 4.25				
C58-53-2 (71°C)	4	4.4	4.2	No Change	4.0	4.3	-10.6	-12.9	58	113
		4.25	4.3 4.2		3.6	4.05 3.55				
C58-56-1 "A" (71°C)	3	3.3	3.7	No Change	3.4	3.0	-12.6	-14.4	97	7.9
		3.9	4.1 3.45		2.65	3.7 2.85				

TABLE XVIII
Effects of Excess Zirconia (30%) on Sterilized Membranes

Sample No.	ft/min	Thickness Before Sterilization		Sample Appearance (Color, physical, mechanical properties and size)	Thickness After Sterilization in Mils			Percent Wt. Change	Specific Resistivity Before Sterilization Ω -in	Specific Resistivity After Sterilization Ω -in
C58-53-2	3	4.3	3.8	KOH clear, sample slight yellow tint	3.2	3.1	-17 (-13.3)	50	24.5 (37)	
		3.6	3.4		2.8	2.9				3.1
C58-53-2	3.5	5.5	5.1	No change	5.2	4.55	-12.9 (-18.4)	50	20 (36)	
		5.6	5.4		4.05	4.0				3.9
C58-53-2	4 (70°C)	5.1	4.8	No change	3.9	3.5	-12.8 (-15.6)	73	28 (125)	
		5.25	5.05		4.4	4.05				4.0
C58-53-2	4 (71°C)	4.6	5.55	No change	4.8	4.6	-12.4 (-12.9)	58	23 (113)	
		5.05	4.4		3.9	3.9				3.55
C58-56-1 "A"	3	4.9	5.4	No change	4.5	3.6	-12.9 (-14.4)	97	34 (7.9)	
		4.7	5.15		4.65	4.2				4.0

TABLE XIX

Sterilization Results on 3 and 12 inch Composites

Sample No.	Coating Speed ft/min	Thickness Before Sterilization in mils.		Sample Appearance (Color, Physical, Mechanical, Properties and Size) After Sterilization	Thickness Before Sterilization in mils.		Wt. Loss Percent	Specific Resistivity Before Sterilization ohm-inch	Specific Resistivity After Sterilization ohm-inch
Pellon 2530	-	5.3	6.0	Sample slight yellow color.	5.9	7.6	0	10	14
		5.4			6.1				
		7.3	5.7		6.6	6.0			
Pellon FT2140	-	6.5	6.3	No change.	6.3	6.0	- 1.08	23	14
		7.1			7.0				
		7.3	6.8		6.5	7.6			
C58-72-2 (Pellon 2140) 3 inch	5	7.6	7.9	No change.	7.2	7.0	- 7.04	60*	18
		7.6			6.8				
		6.95	6.3		6.8	7.0			
C58-72-2 (Pellon 2140) 3 inch	6	8.6	7.25	No change.	7.2	8.1	- 7.0	30*	11
		8.95			9.1				
		8.6	9.2		8.6	7.3			
C58-72-2 (Pellon 2140) 3 inch	7	8.9	8.1	No change.	6.8	8.0	- 7.3	25*	13
		7.55			6.9				
		6.8	7.7		8.0	7.3			
C58-73-1 (Pellon 2140) 12 inch	5	8.4	9.0	No change.	7.3	8.1	- 7.92	75*	7
		9.4			9.05				
		9.7	9.55		9.3	9.3			
C58-73-1 (Pellon 2140) 12 inch	6	8.05	7.0	No change.	7.5	7.5	- 7.6	13*	3.5
		7.5			7.0				
		7.1	7.6		7.1	5.9			
C58-74-1** (Webrii EM476) 12 inch	5	5.5	5.3	No change.	5.4	4.4	- 9.87	120	22
		5.5			4.5				
		4.3	4.5		4.15	3.8			
C58-74-1** (Webrii EM476)	6	5.1	5.5	No change.	4.0	4.3	-10.2	69	33
		4.6			4.5				
		4.8	5.0		4.4	4.45			
C58-75-1** (Webrii EM476) 12 inch	5	7.1	6.9	No change.	6.05	6.1	-10.2	32	17
		5.9			5.7				
		5.9	5.6		5.4	5.8			
C58-75-1** (Webrii EM 476) 12 inch	6	6.9	6.0	No change	6.6	5.5	- 9.75	41.5	20
		6.65			6.1				
		6.7	6.1		6.4	5.7			

* The initial resistance of these samples was generally high; soaking overnight in 40% KOH gave the resistance values reported in this table.

**These samples were sterilized for 89 hours instead of the usual 60 hours.

TABLE XX

Sterilization Results on 12 inch Wide Pellon 2140 - and Webril EM 476 -
Containing Composites

Sample No.	Coating Speed, ft./min.	Thickness After Sterilization in Mils		Sample Appearance (color, physical, mechanical properties and size). After sterilization.	Thickness After Sterilization in Mils		Percent Weight Change	Specific Resistivity Before Sterilization Ω -inch	Specific Resistivity After Sterilization Ω -inch
C58-75-2 EM476	5.5	4.55	4.65	No Change	4.05	4.7	- 8.8	113**	28*
		5.1			4.7				
		4.4	5.0		4.8	4.7			
C58-76-1 EM476	4.5	5.0	5.1	No Change	3.7	3.6	-10.3	> 150*	19*
		5.1			4.9				
		4.7	4.7		4.8	4.85			
C58-76-1 EM476	5.5	6.4	5.4	No Change	5.8	6.1	- 8.2	> 150*	16*
		5.6			5.0				
		5.15	5.2		4.6	4.6			
C58-76-1 EM476	6.0	5.0	5.75	No Change	3.9	3.5	-14.6	> 150*	13*
		4.8			4.4				
		5.4	6.65		5.3	5.1			
C58-77-1 EM476	5.0	5.1	4.7	No Change	4.9	4.6	- 7.46	78*	12*
		4.7			4.3				
		4.4	4.4		3.85	4.0			
C58-77-1 EM476	6.0	4.3	4.8	No Change	4.1	4.3	-19.9	84*	13*
		4.4			3.9				
		4.3	4.6		3.8	3.4			
C58-77-2 EM476	5.5	3.4	3.6	No Change	2.9	2.7	- 9.83	51*	34*
		3.6			3.3				
		4.5	4.4		3.8	3.8			
C58-78-1 Pellon 2140	5.0	8.6	7.8	No Change	7.25	6.5	- 6.3	> 105*	9*
		8.3			7.5				
		6.8	7.8		6.6	6.8			

* These values were obtained after exposing the sample to the KOH in the cell for 0.5 hr. without appreciable change in resistance.

** This value was obtained on exposing the sample to the KOH in the cell for approximately 8 hrs., because the one half hour exposure showed appreciable change in resistance.

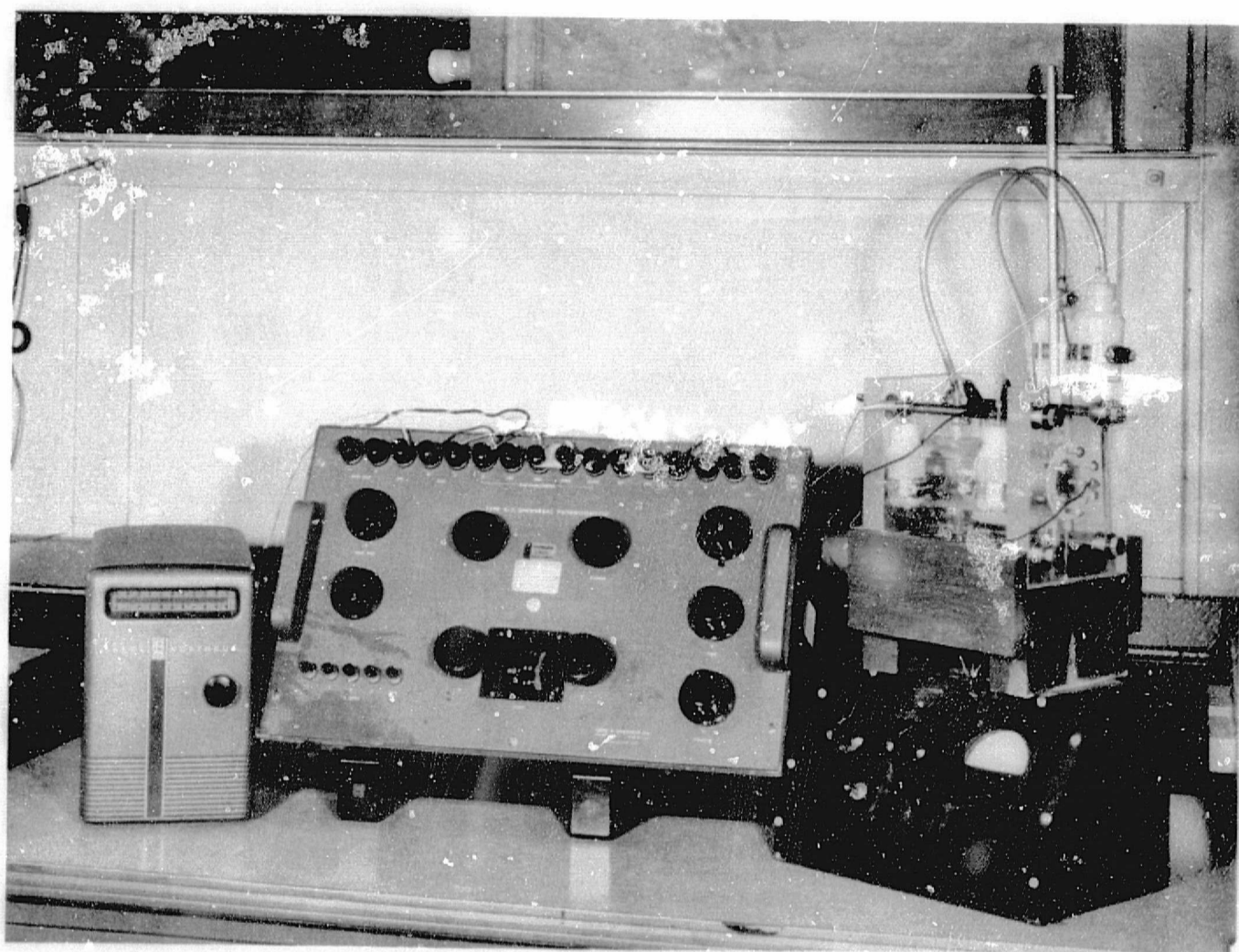


Figure 1 — Resistivity tester, dc current method.

Dwg. 852A384

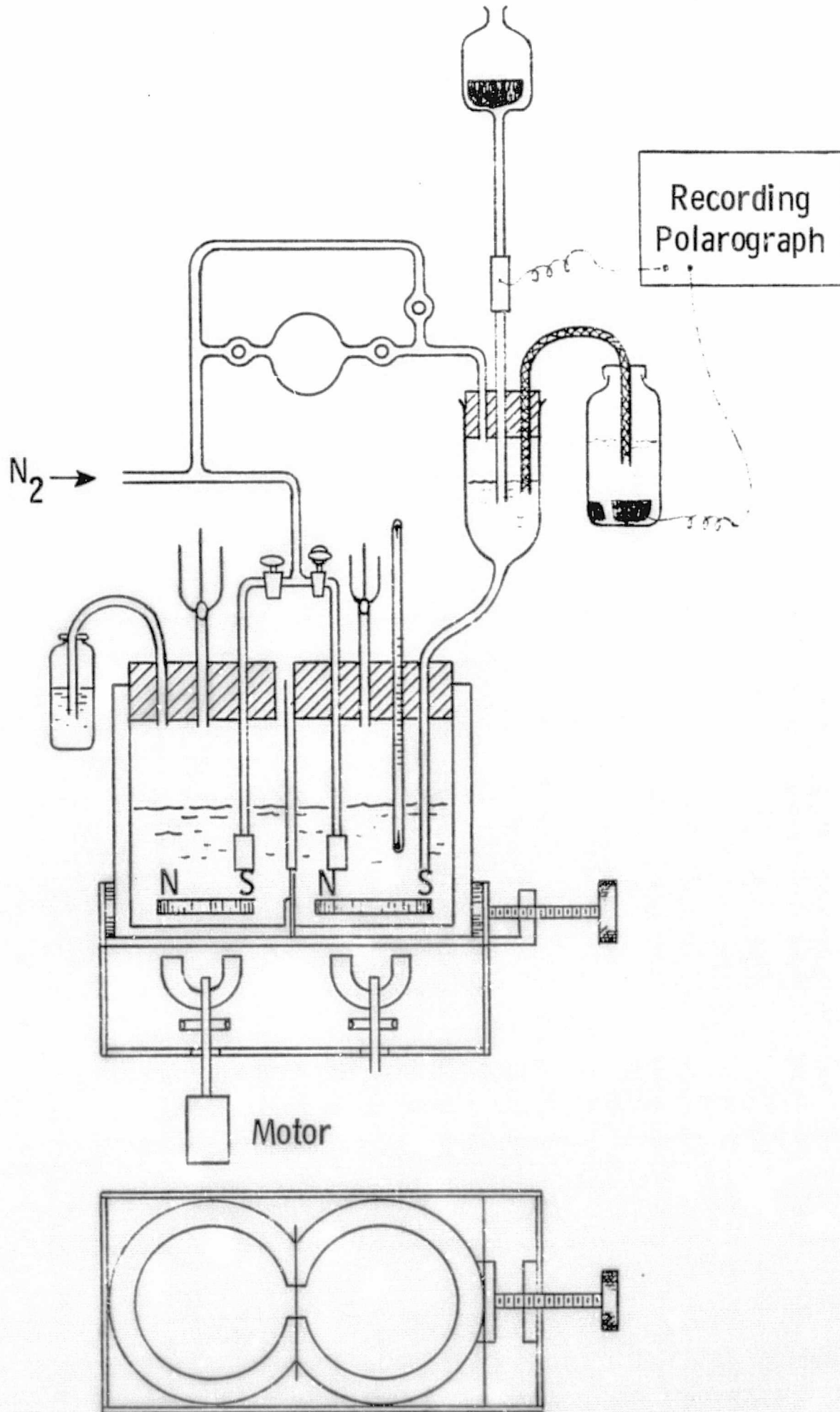


Fig. 2—Diffusion testing apparatus with polarographic sensing

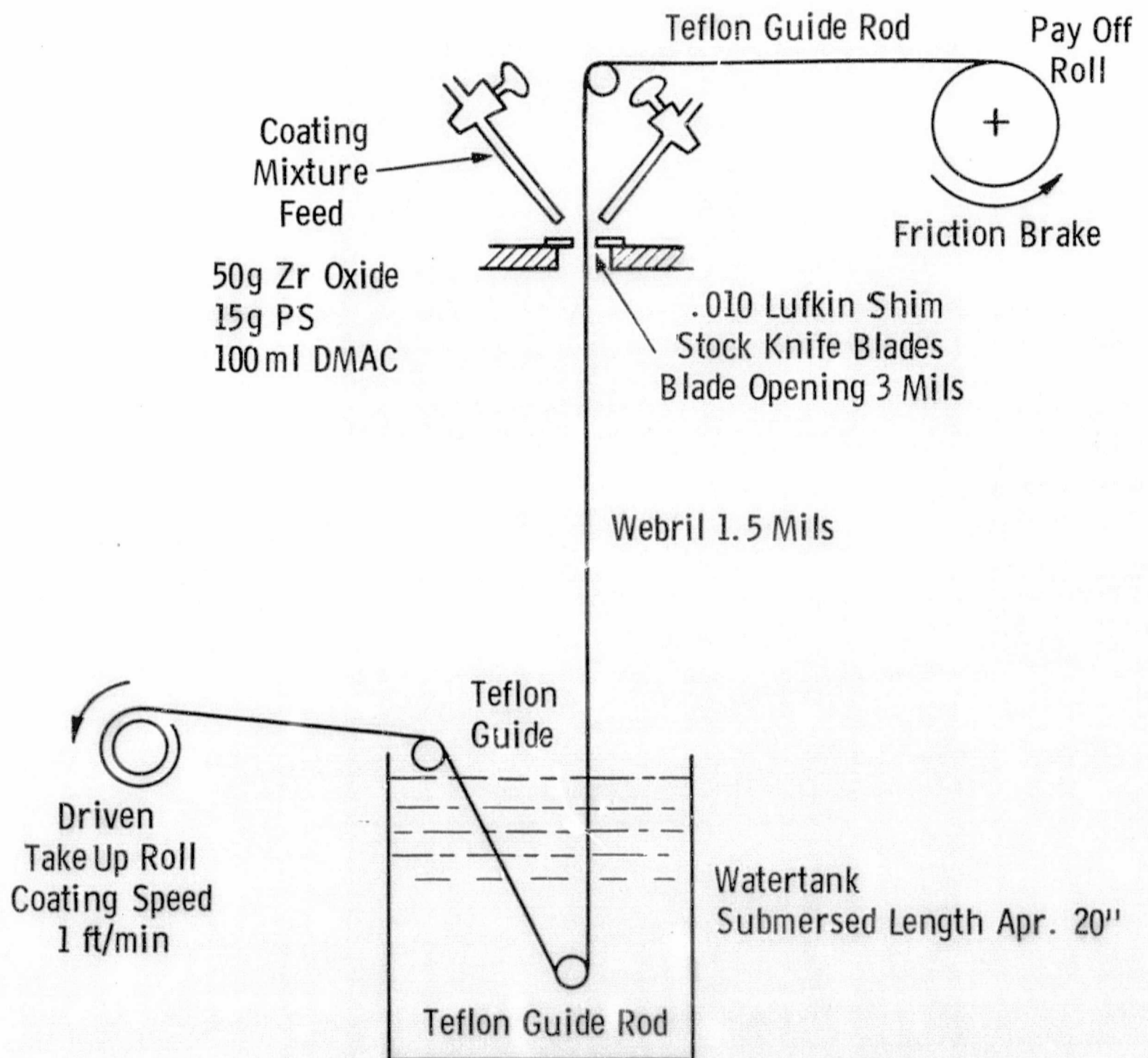
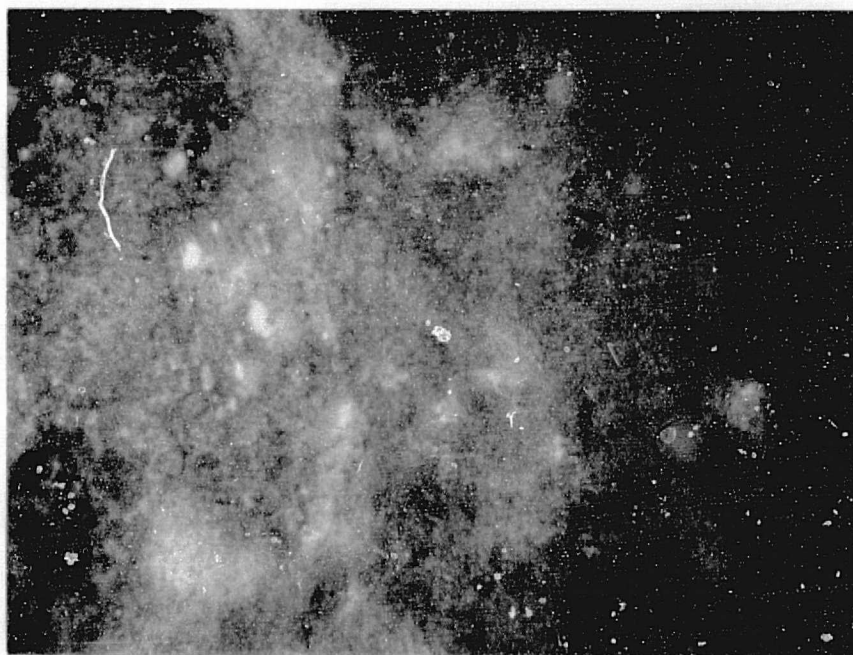
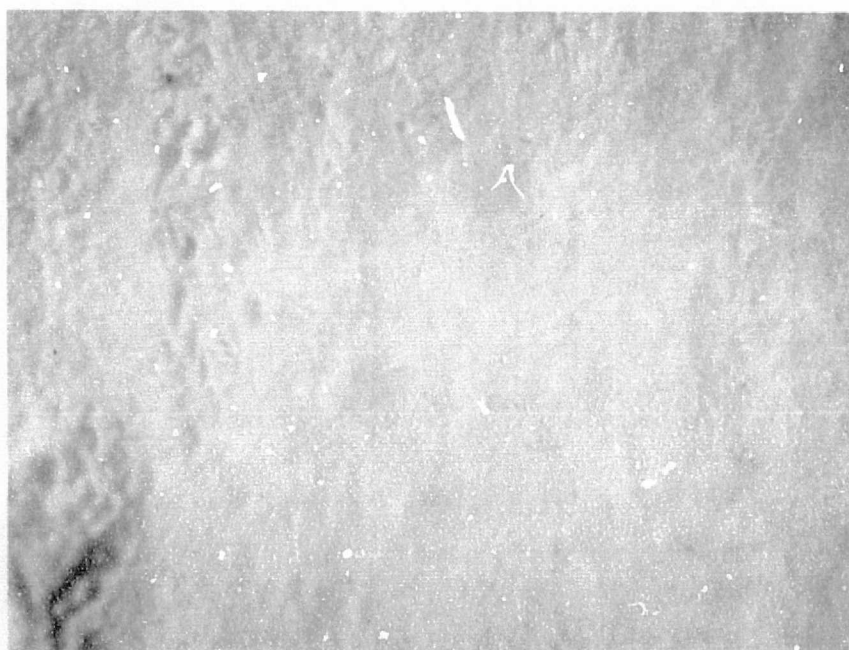


Fig. 3-Continuous coating machine



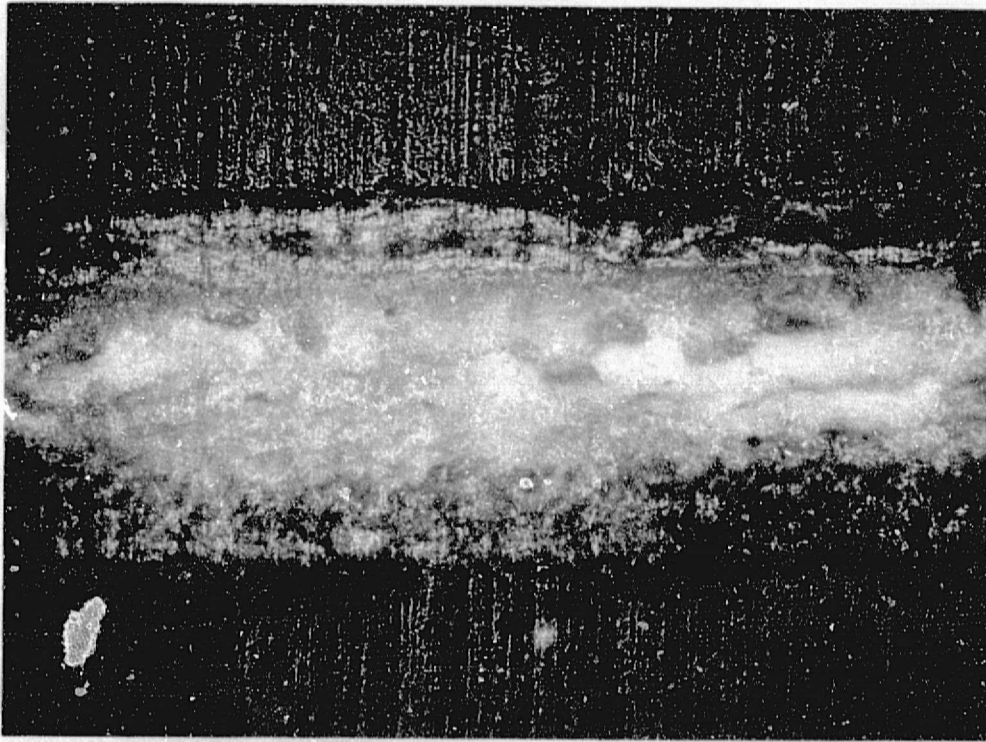
Transmitted Light 22X



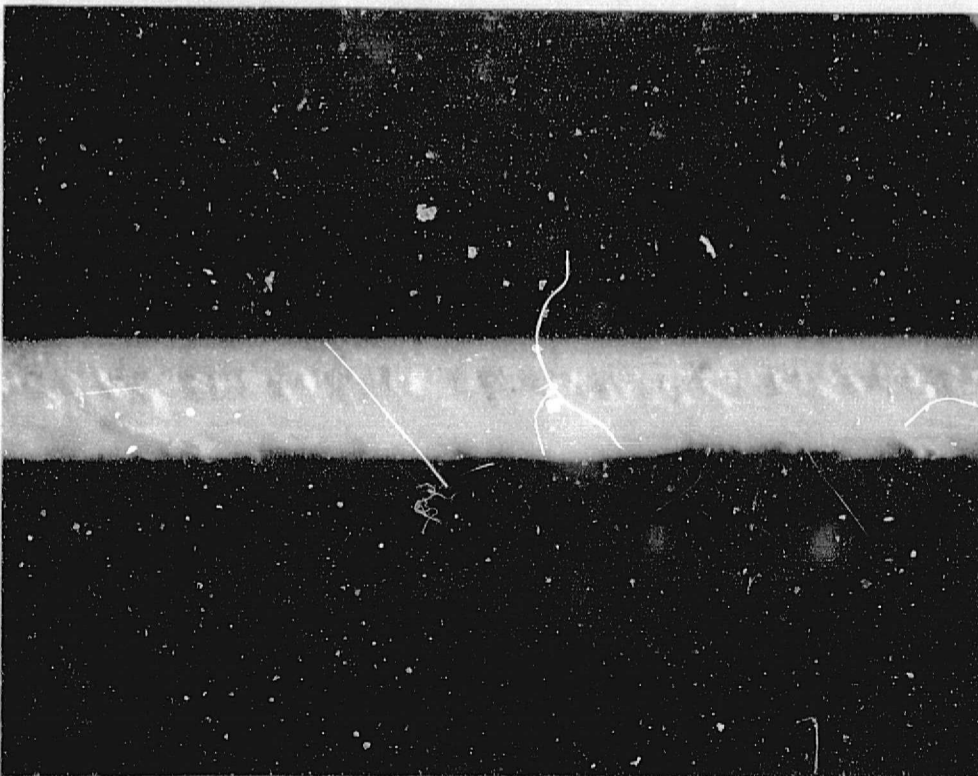
Reflected Light 22X

Filler Distribution in Membranes

Fig. 4 - Sample No. 58-9-27-1. Polysulfone polymer binder, $Zr(OH)_4$ filler, 2 layers 1.5 mil each thick, Polypropylene Webril



200 X



100 X

Cross Sections of Membrane 83-11-17-2

6.3 mil thk. water cast

Polysulfone without filler

Fig. 5

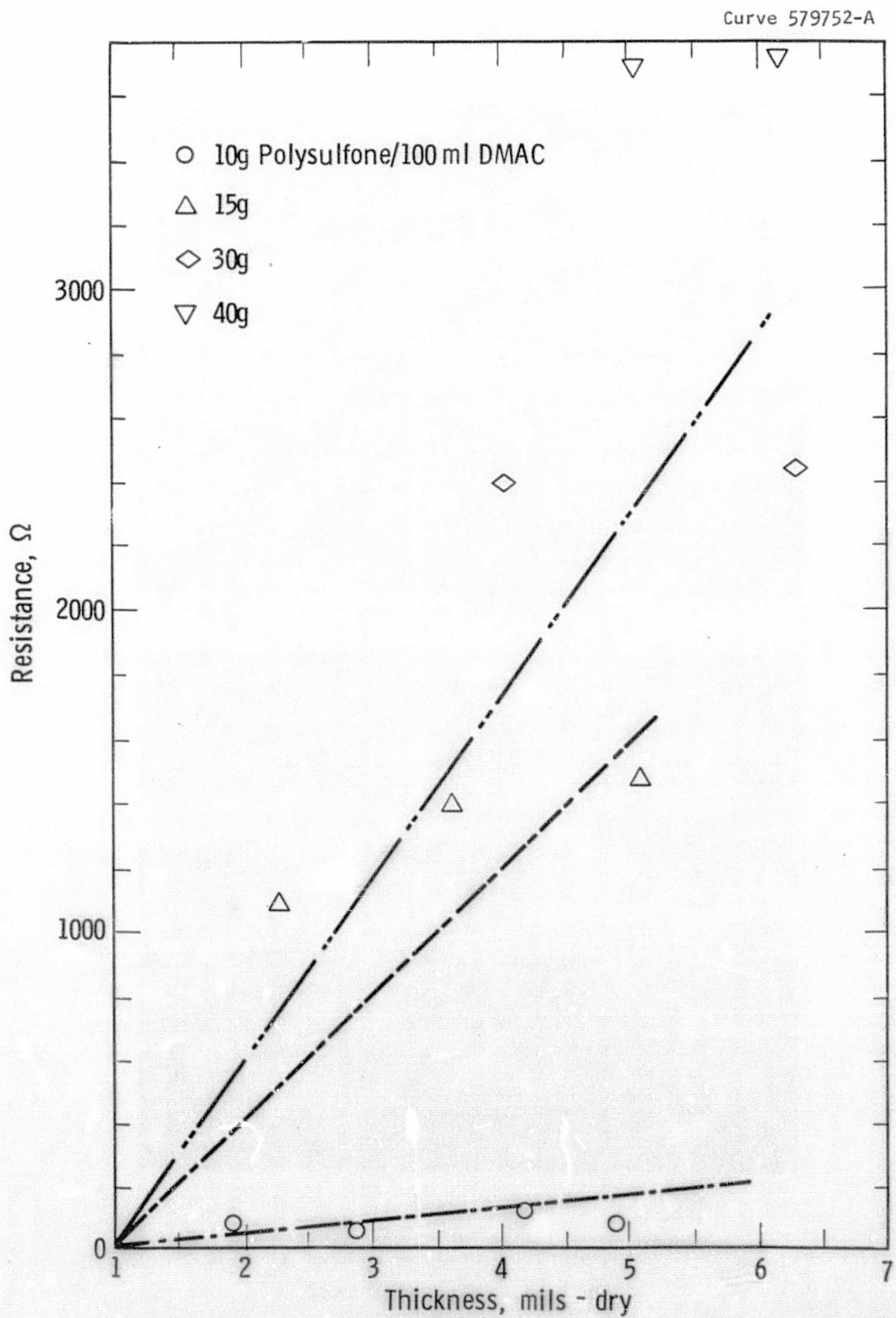


Fig. 6—Resistance vs film thickness for various polymer concentrations

Curve 579753-A

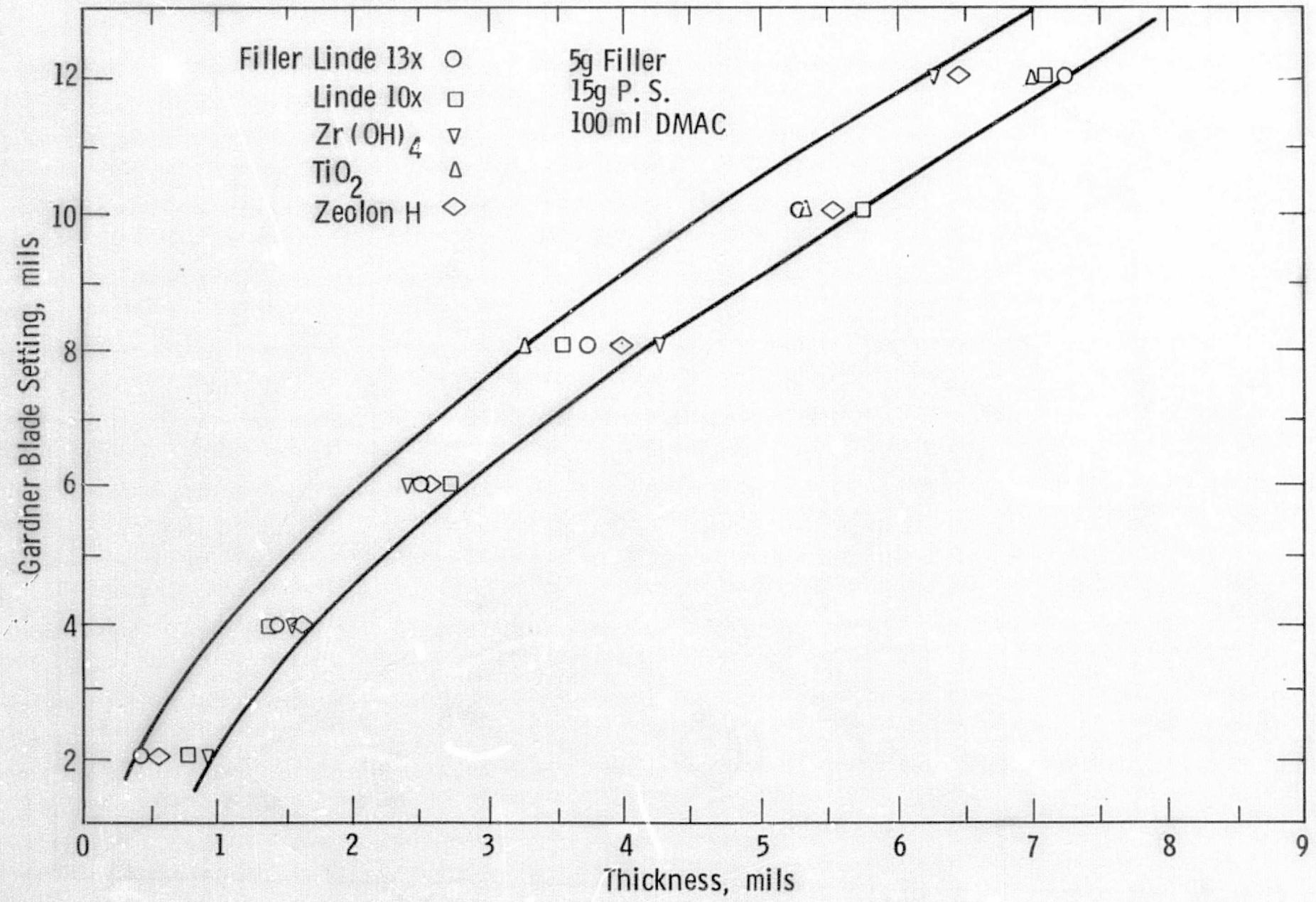


Fig. 7—Blade setting vs dry film thickness with different fillers

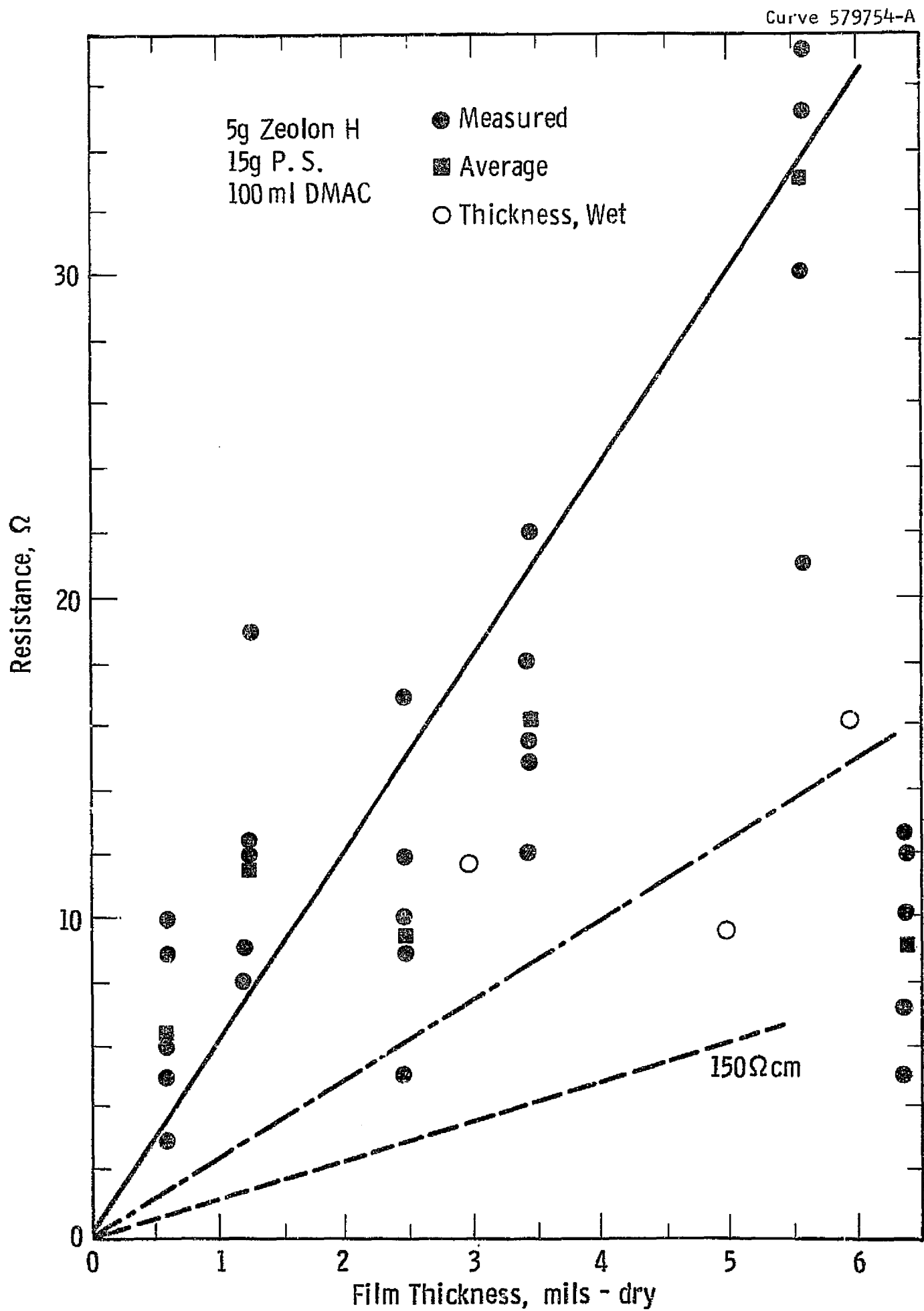


Fig. 8 - Resistance vs film thickness with Zeolon H as fillers

Curve 579755-A

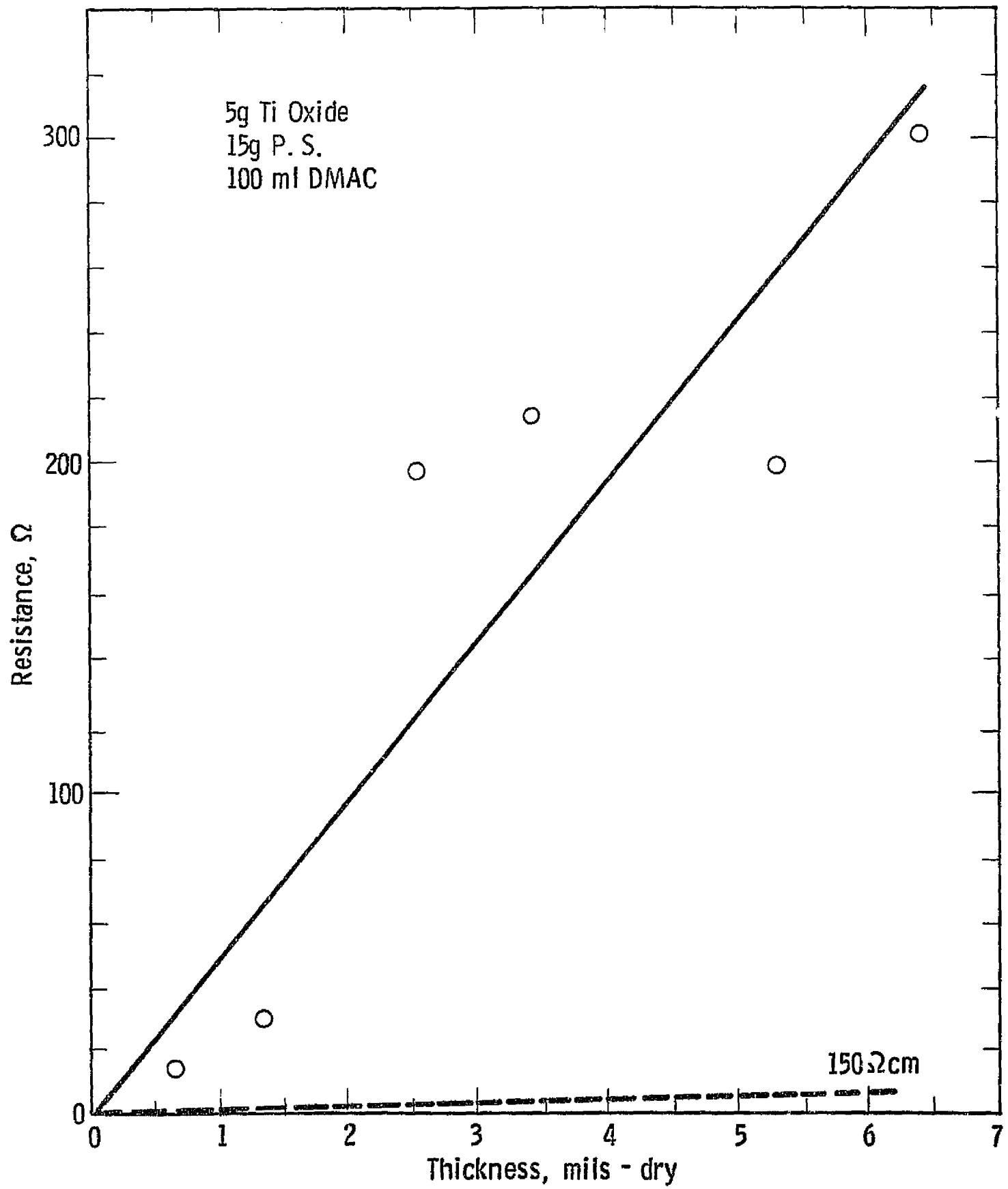


Fig. 9 - Resistance vs film thickness with Ti oxide as filler

Curve 579756-A

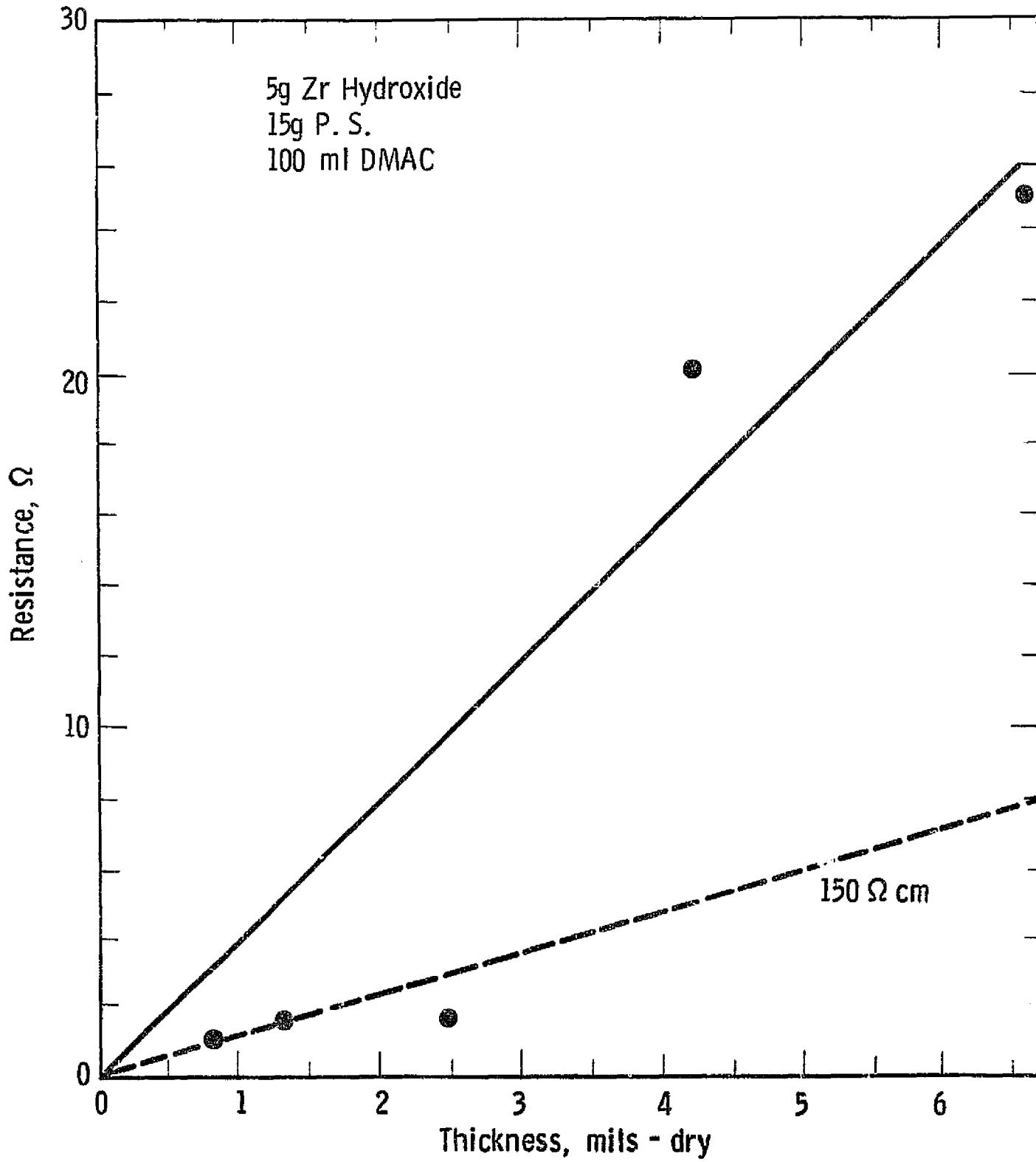
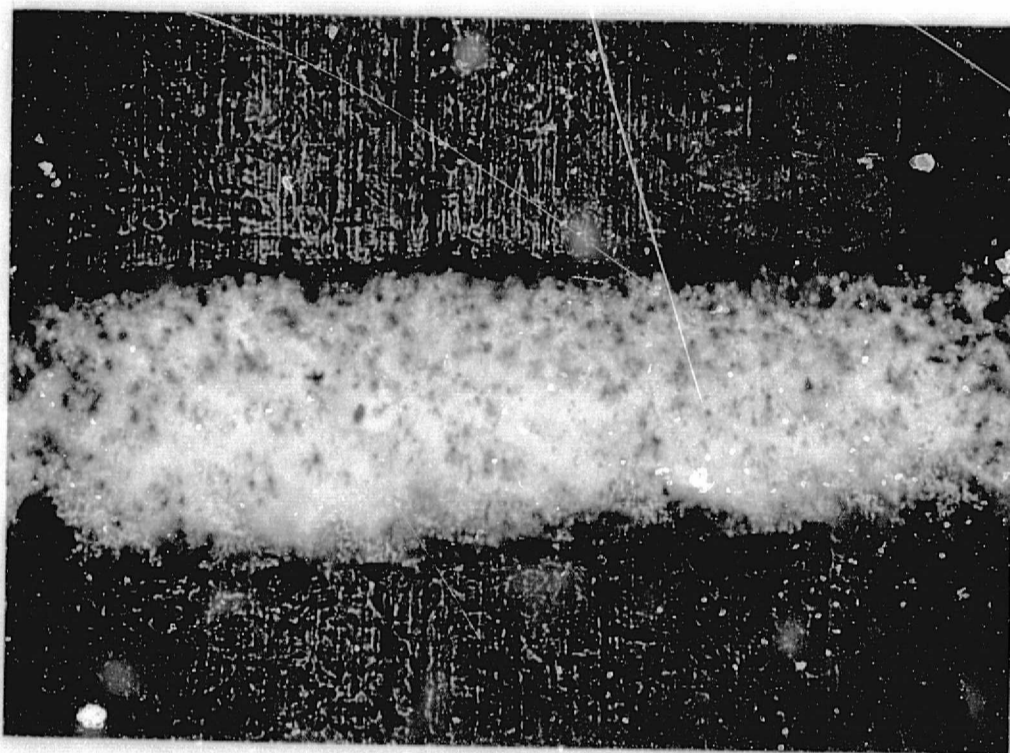
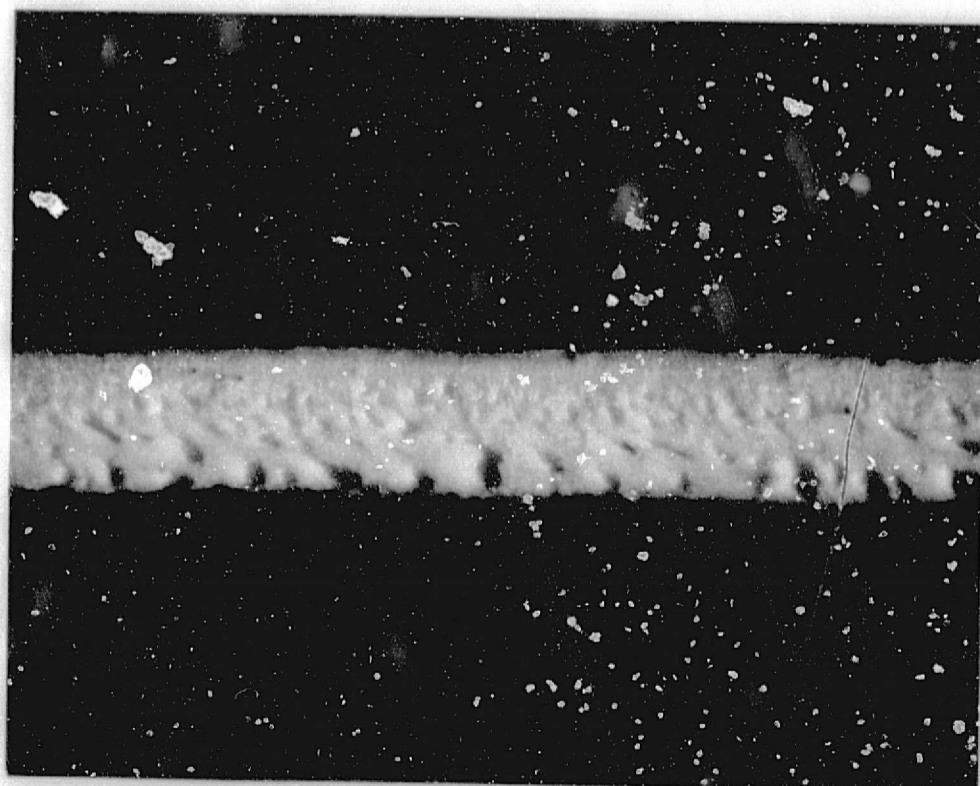


Fig. 10—Resistance vs film thickness-zirconium hydroxide as filler



200 X



100 X

Cross Sections of Membrane 07-11-29-3

6.3 mil thk. water cast

Polysulfone with 25% filler by weight ($Zr(OH)_4$)

Fig. 11

Curve 579757-A

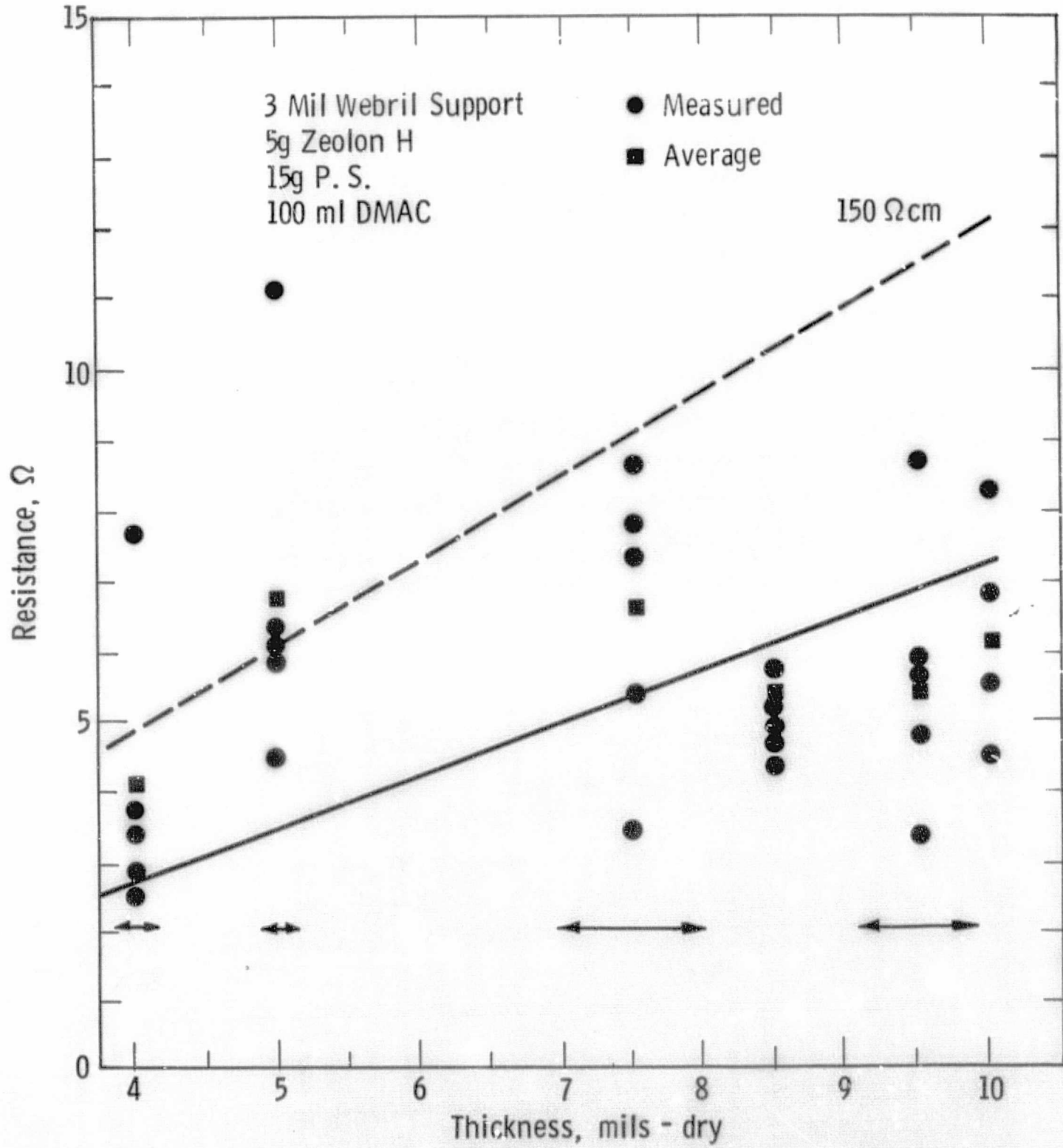


Fig. 12—Resistance vs film thickness with zeolon H as filler on Webril

Curve 581045-A

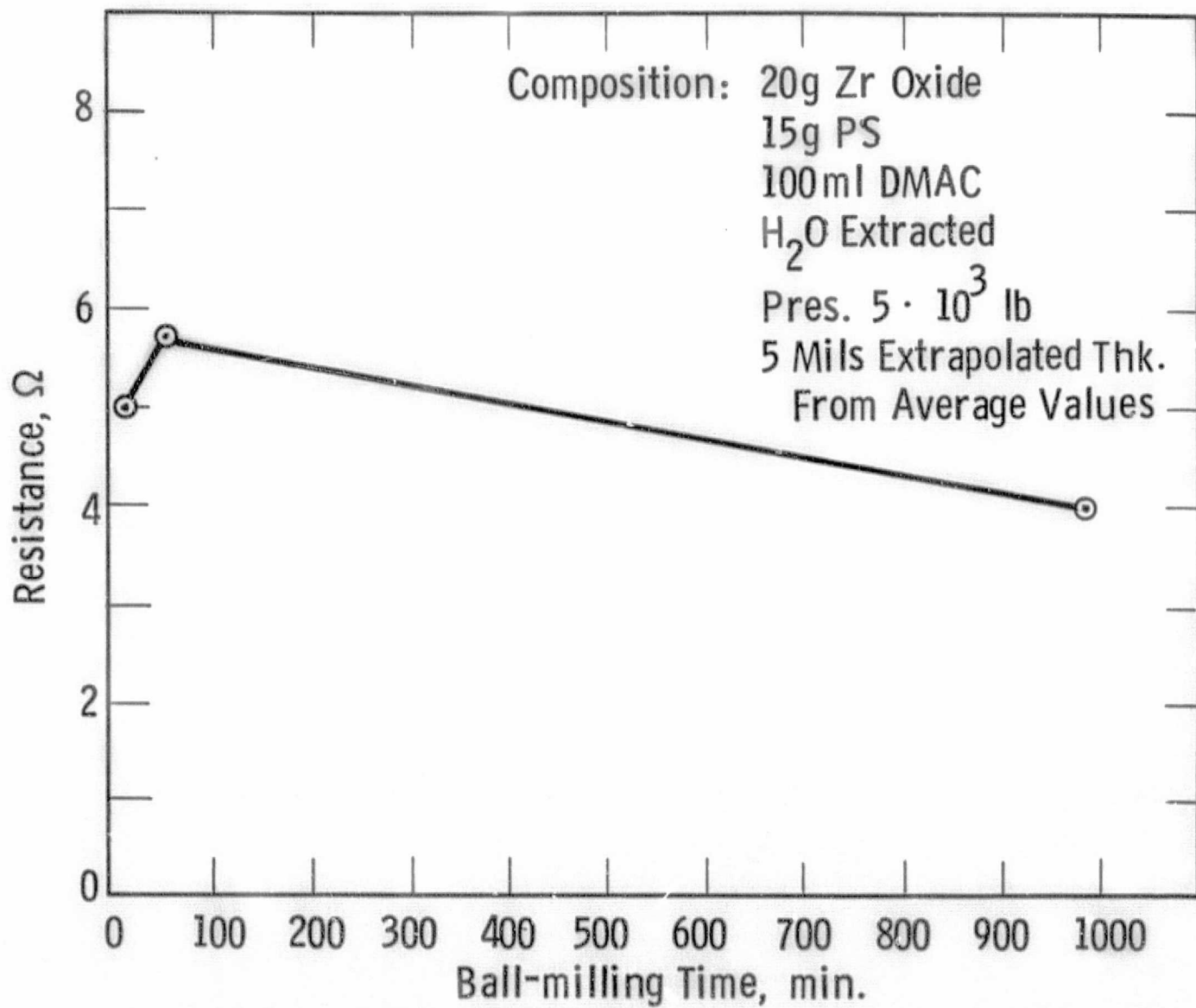


Fig. 13—Relation between ball-milling time and resistance

Curve 581047-B

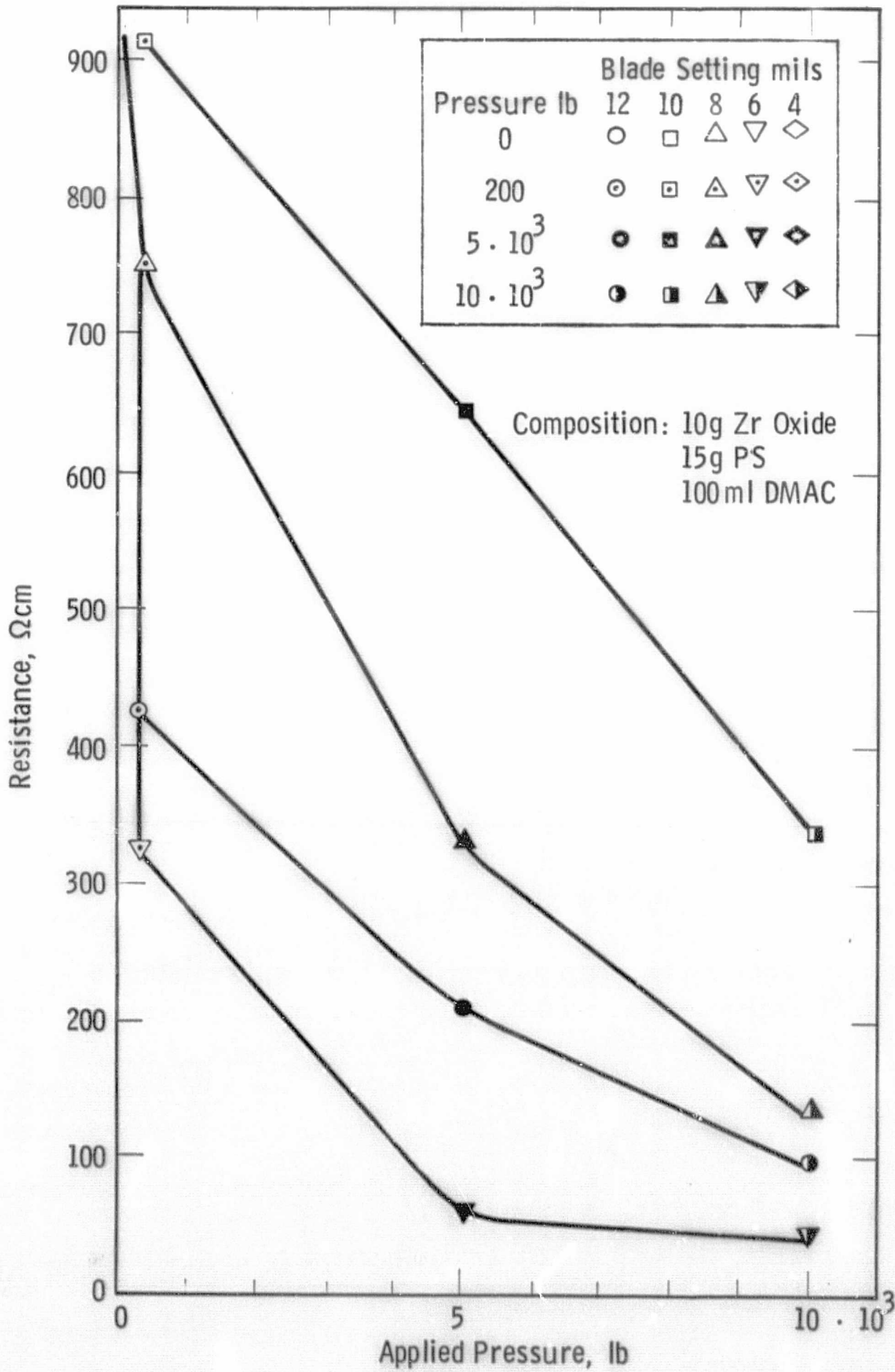


Fig. 14—Relation between compression pressure and resistivity of films.
Low oxide loading

Curve 581046-A

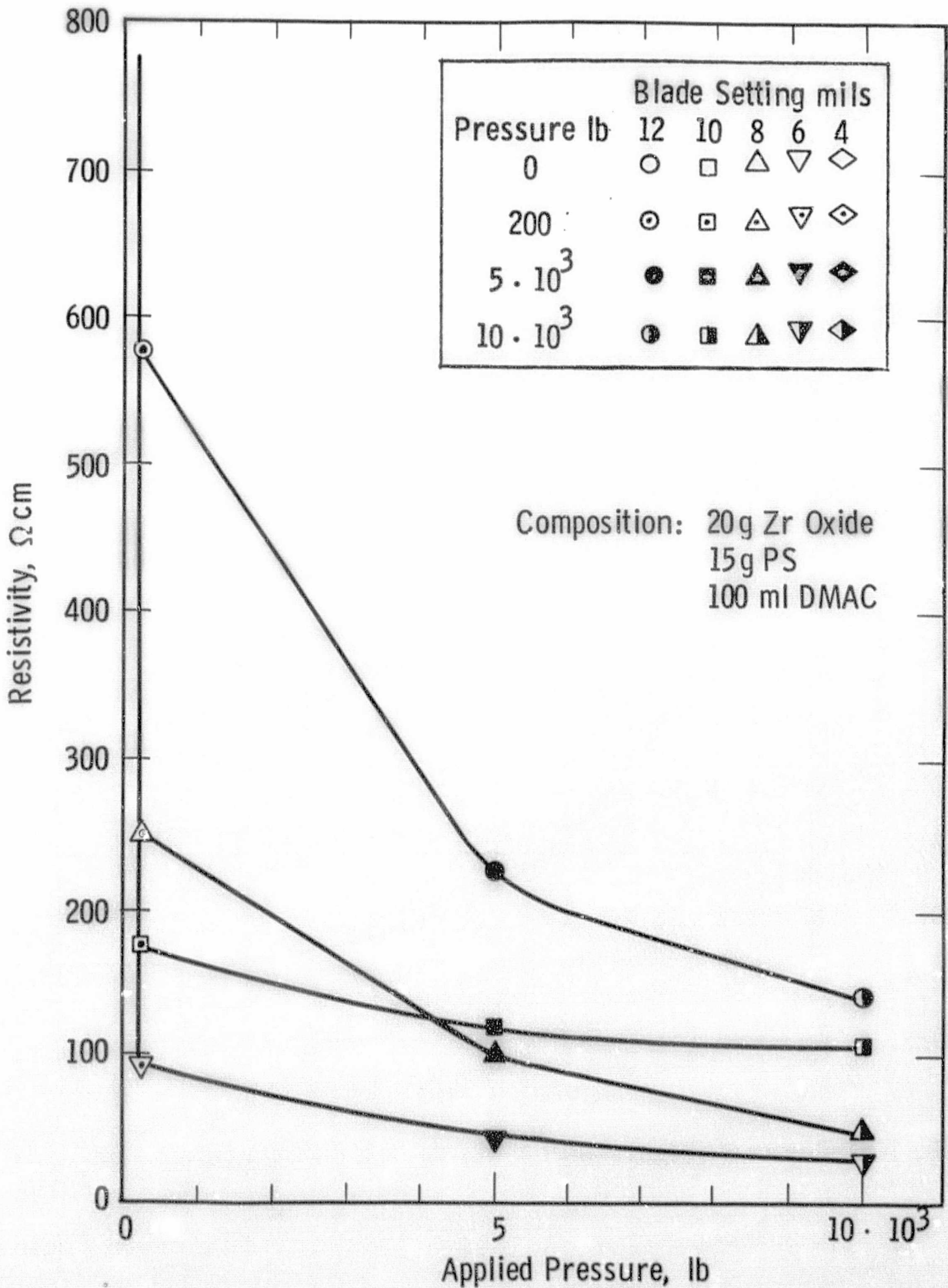


Fig. 15—Relation between compression pressure and resistivity of films. High oxide loading

Curve 581042-A

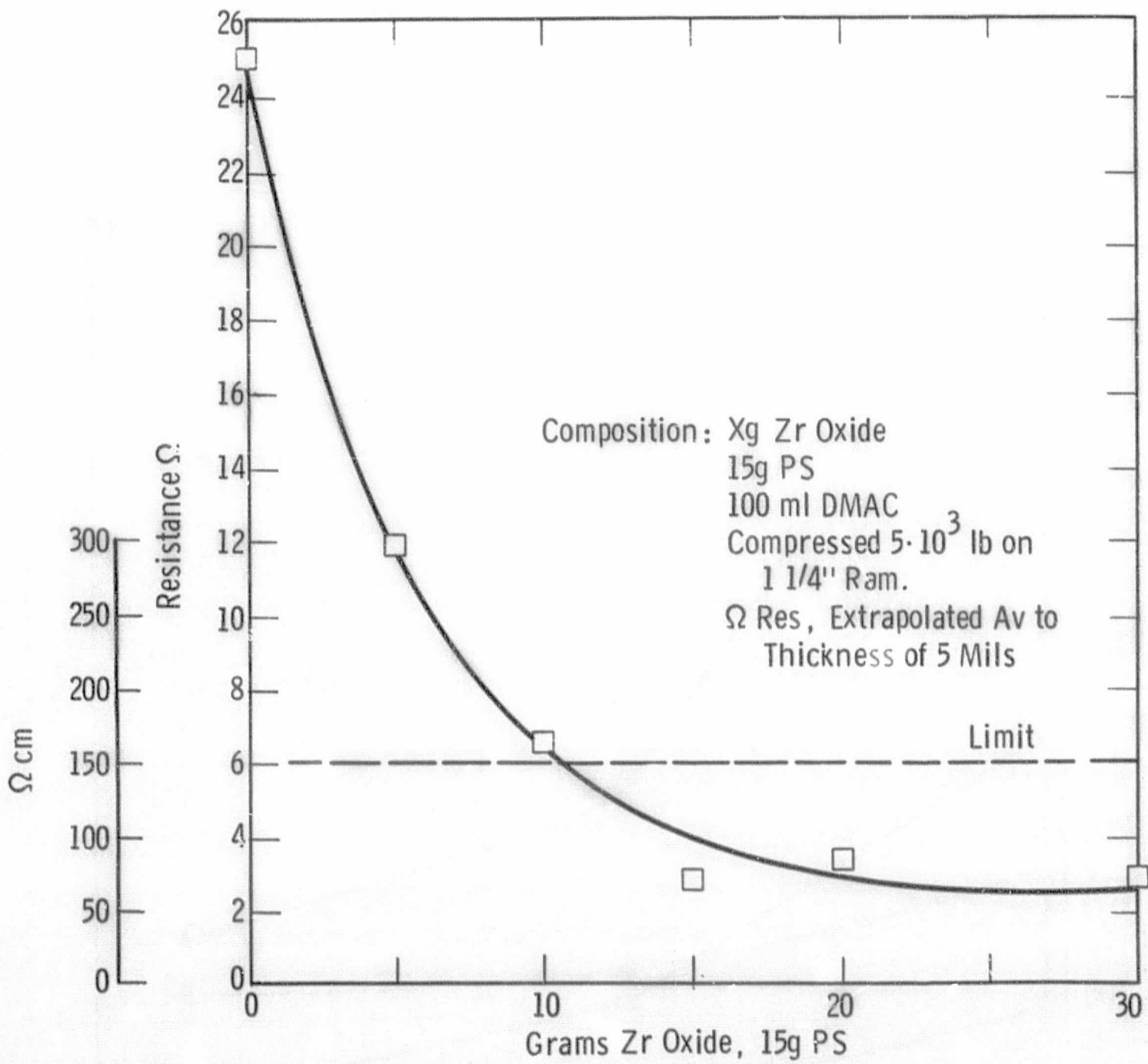


Fig. 16—Influence of amount of filler on resistance of films pressed at 5×10^3 lb

Dwg. 852A909

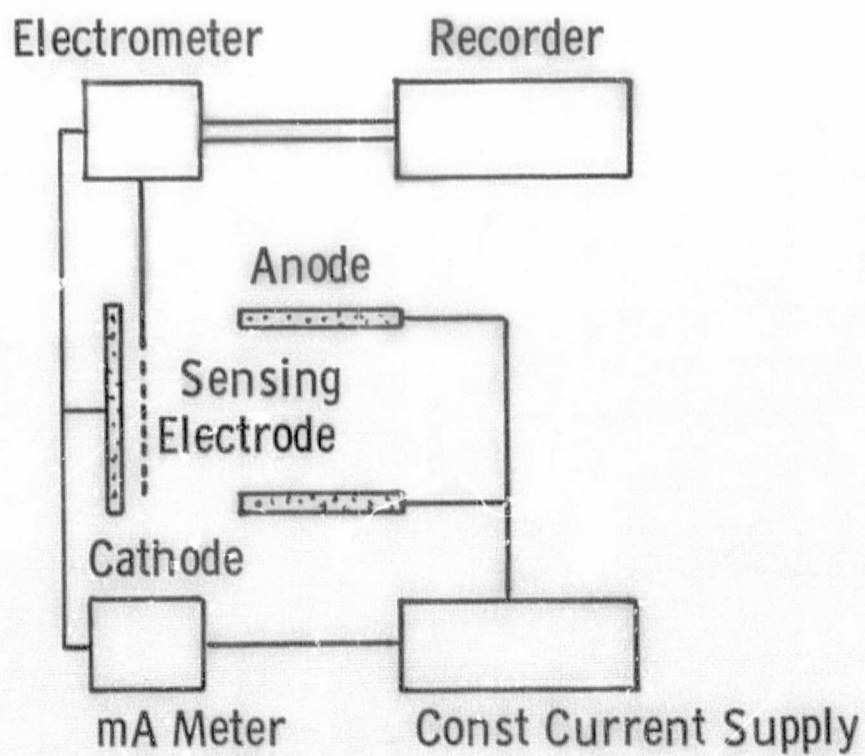
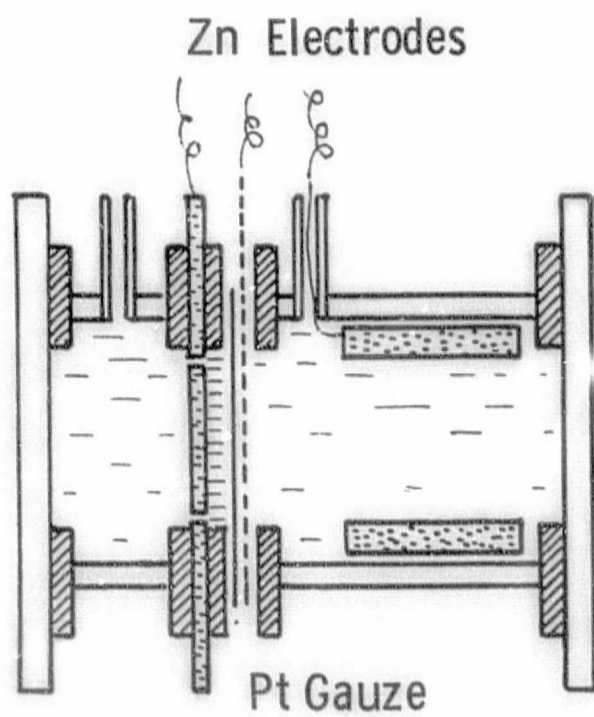


Fig. 17 - Dendrite penetration tester

Curve 579870-A

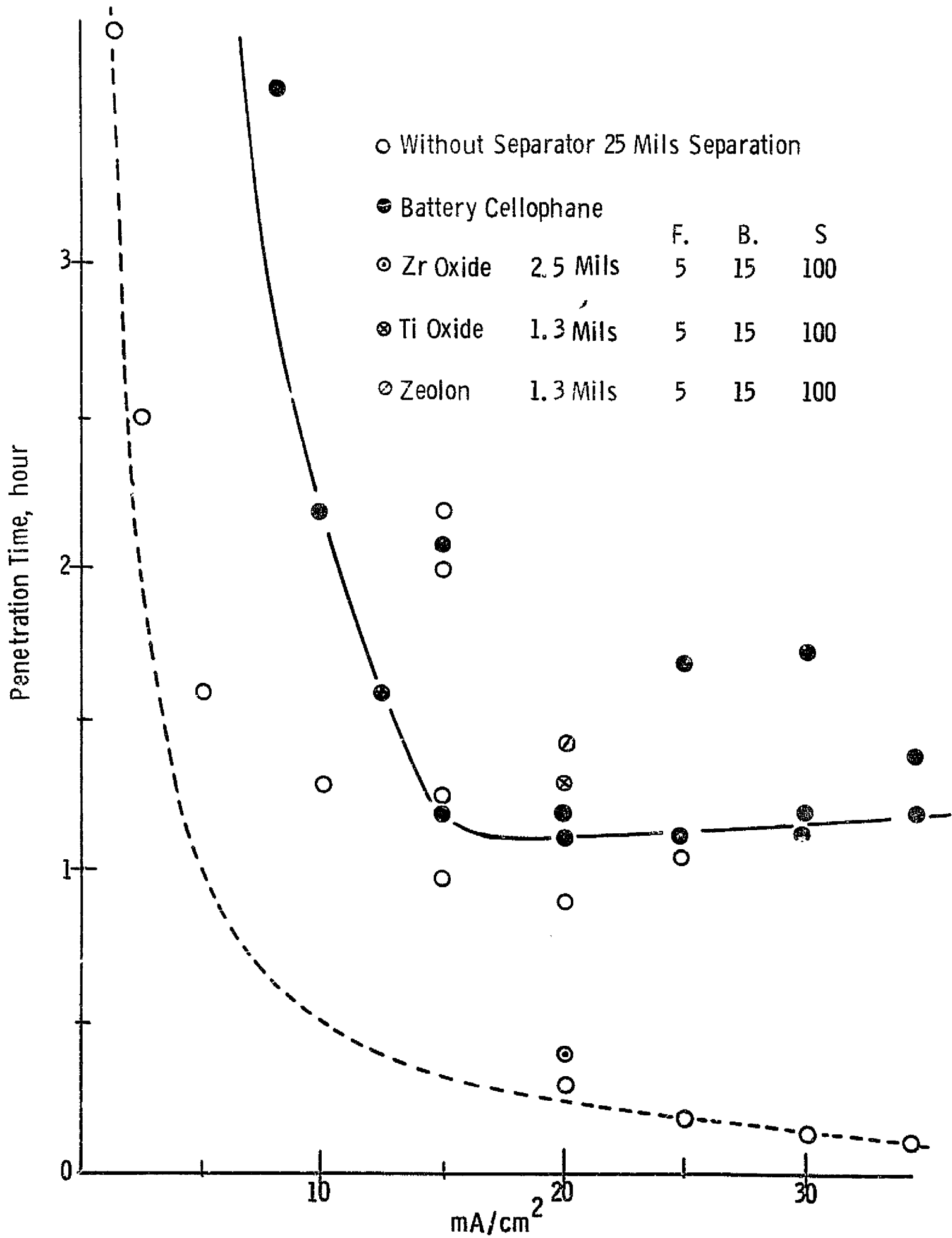


Fig. 18-Dendrite penetration time - current density relations

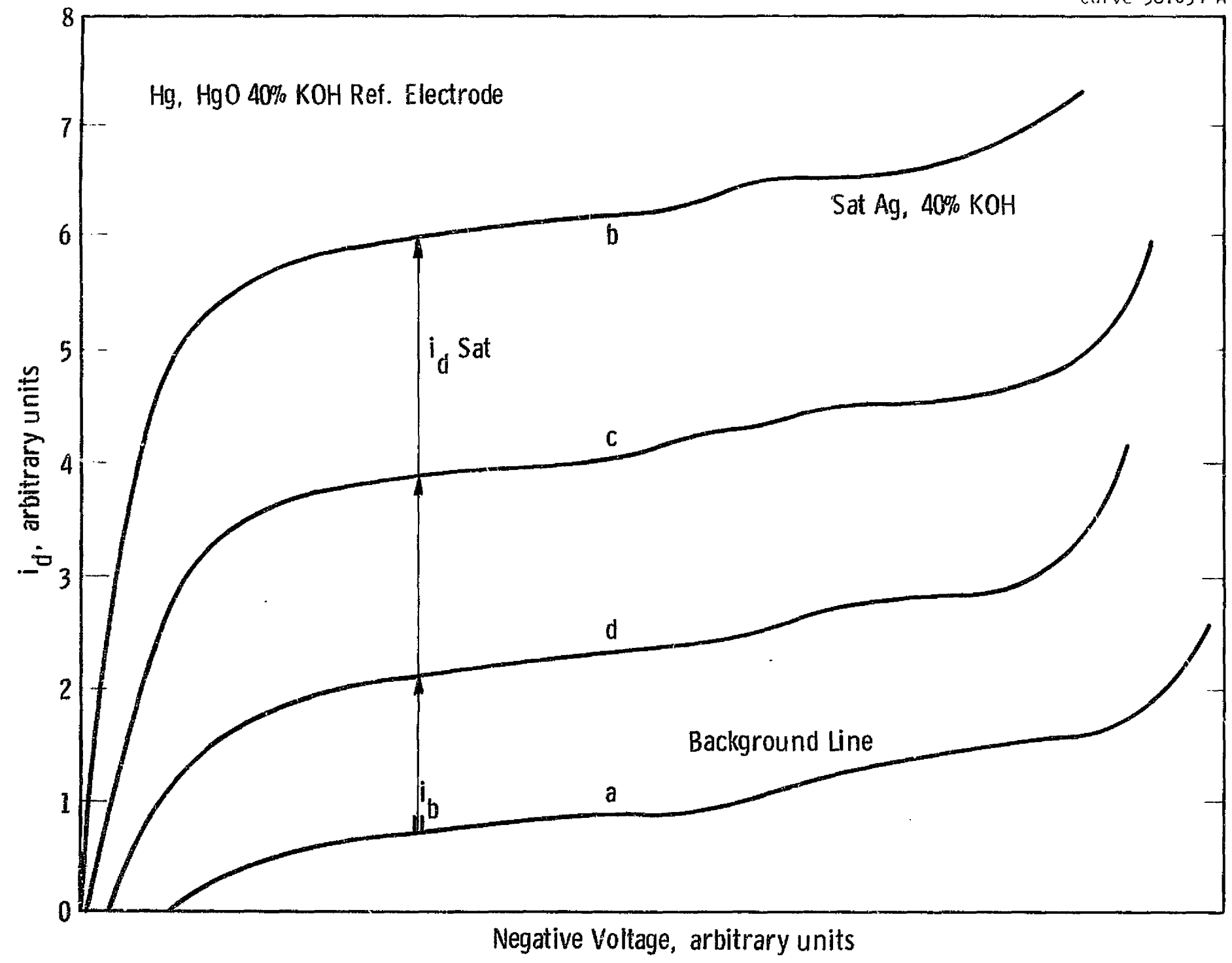


Fig. 19—Polarograms of different silver concentrations

Curve 581033-A

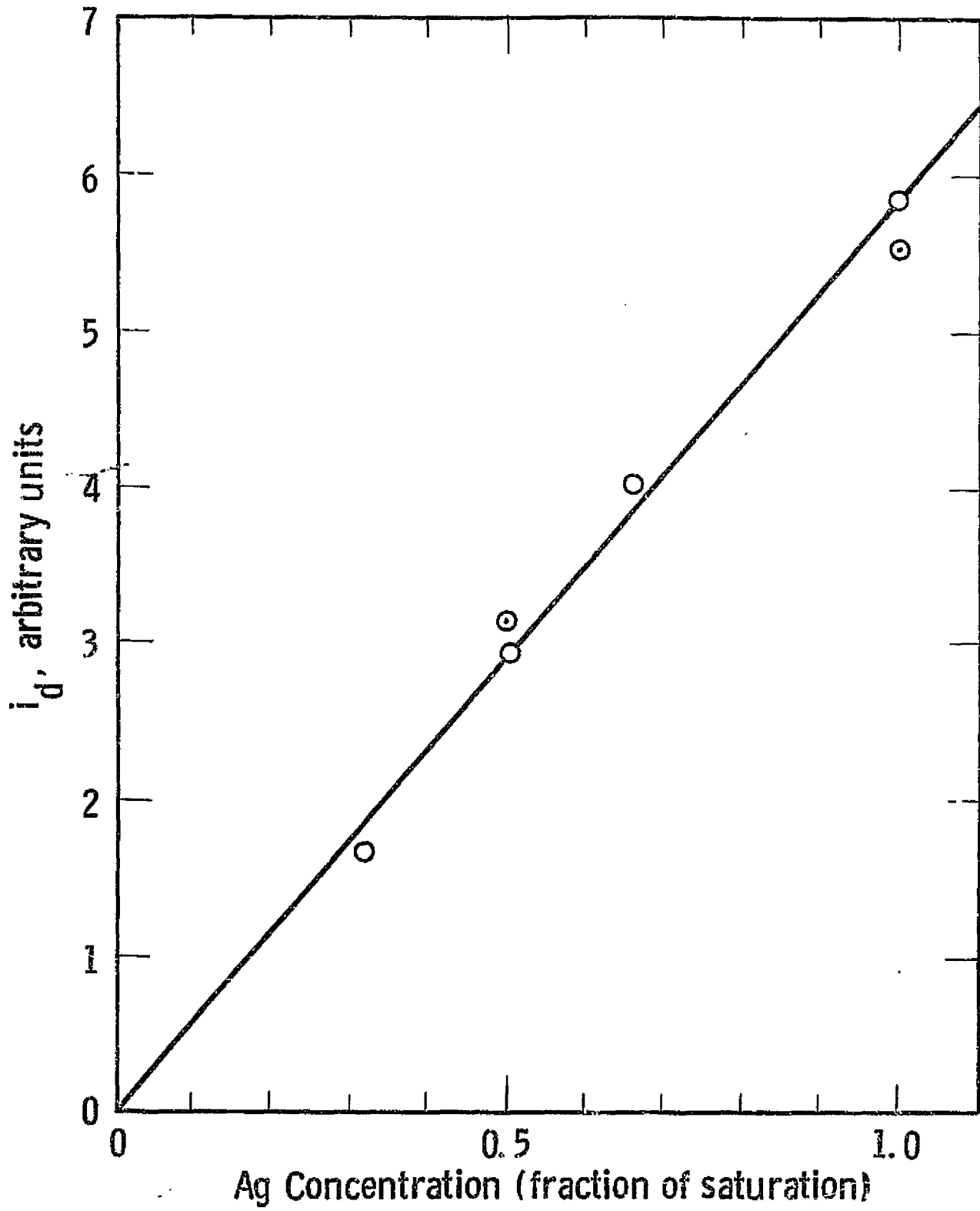


Fig. 20 - Relation between i_d and silver concentration

Curve 581039-A

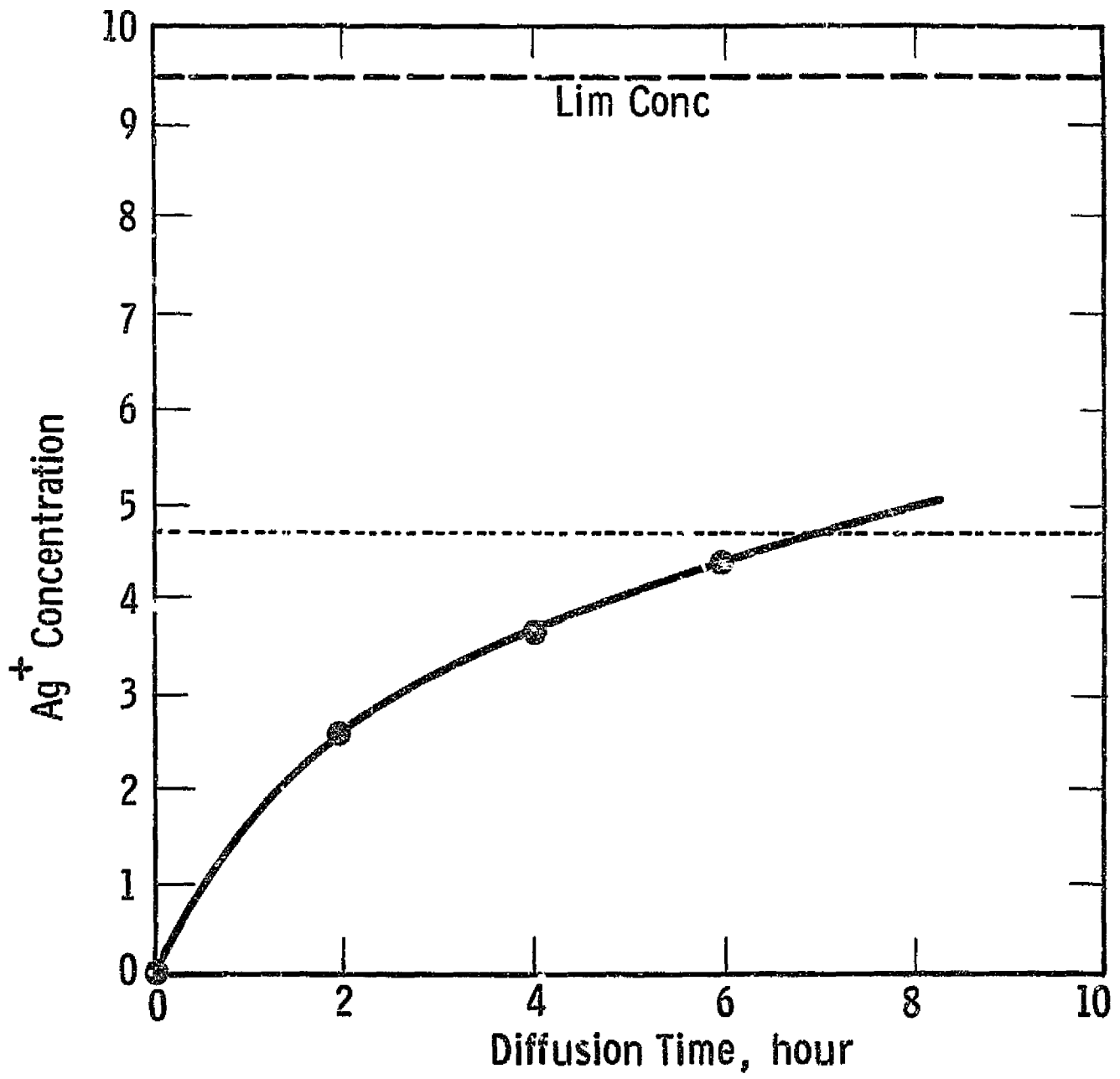


Fig. 21 - Relation between silver concentration i_d and diffusion time in hour

Dwg. 854A239

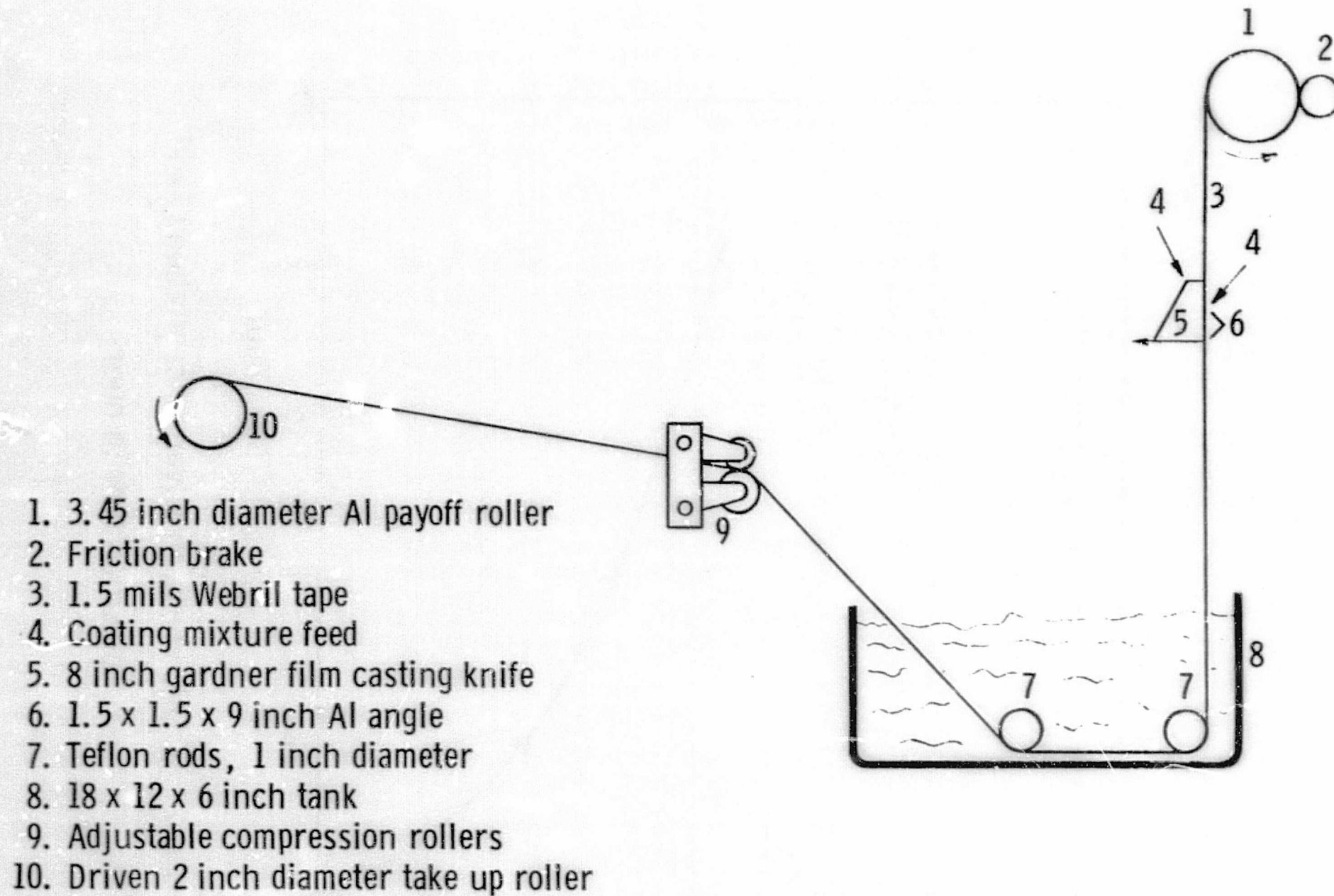


Fig. 22—Laboratory size continuous coating machine

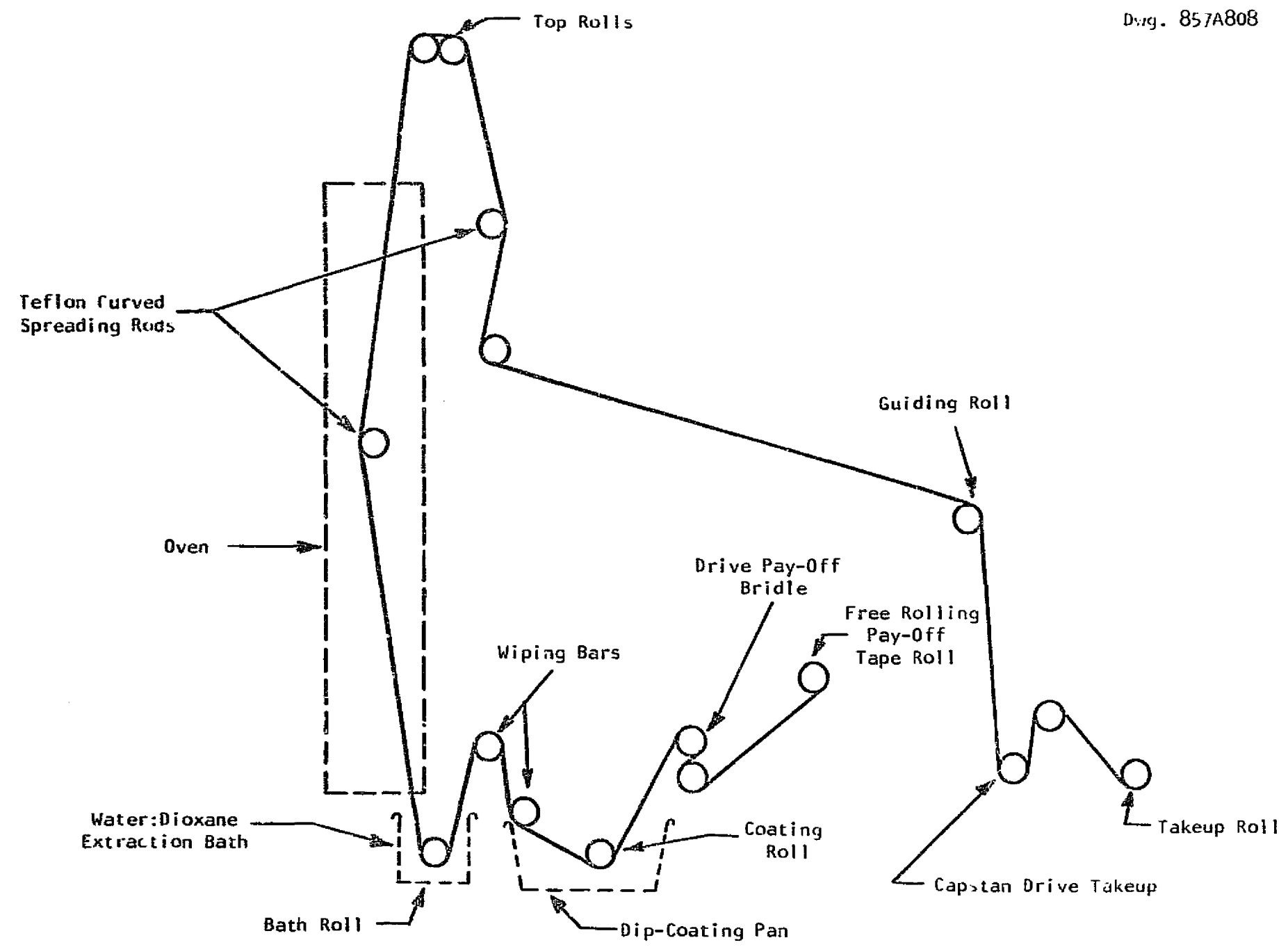


Fig. 23—Set-up for continuous coating of 1-foot wide tape in industrial tower

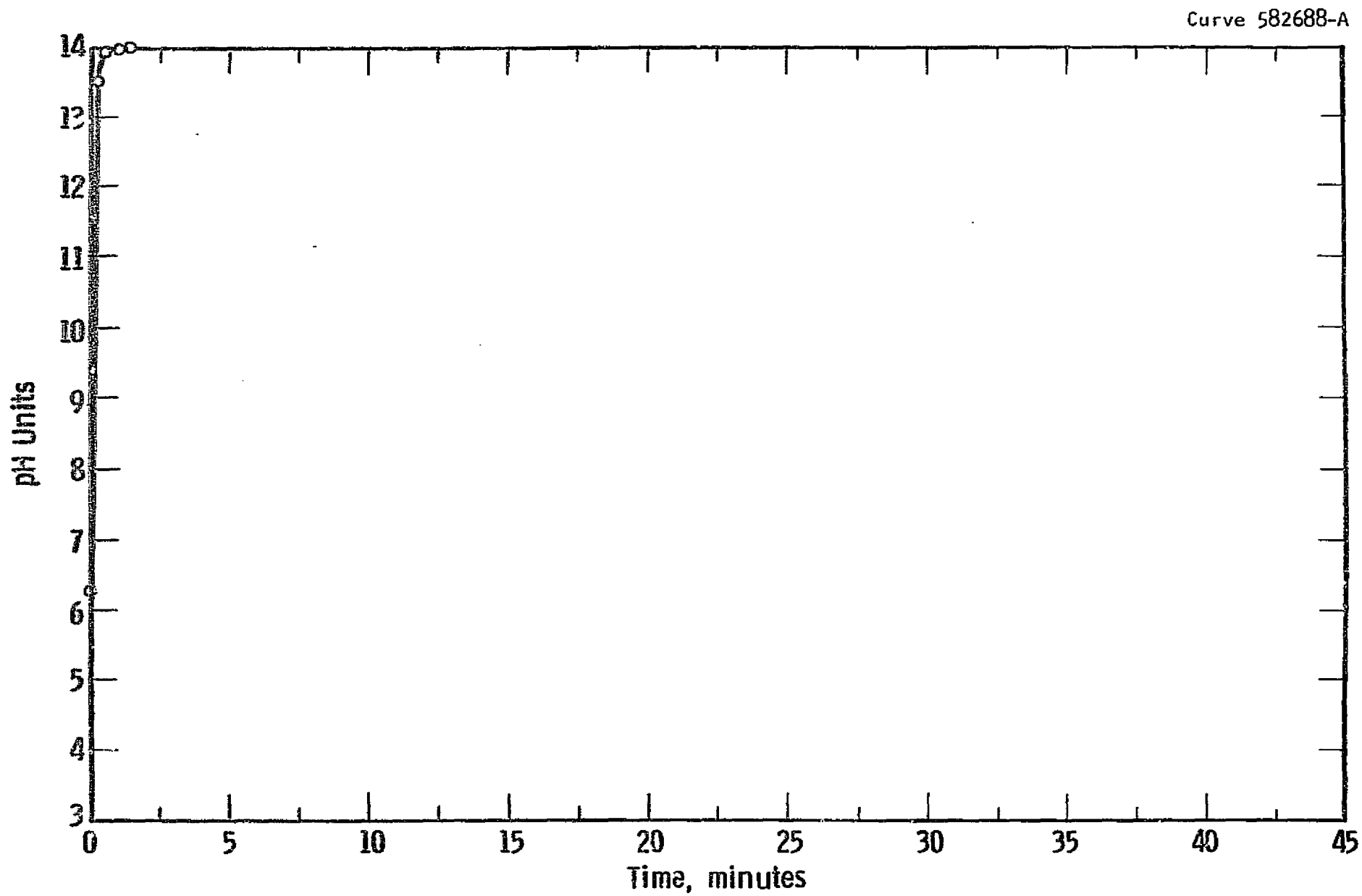


Fig. 24—Electrolyte diffusion time, 40% KOH, 26°C. Bare Webril tape, ave. thickness 1.91 mils

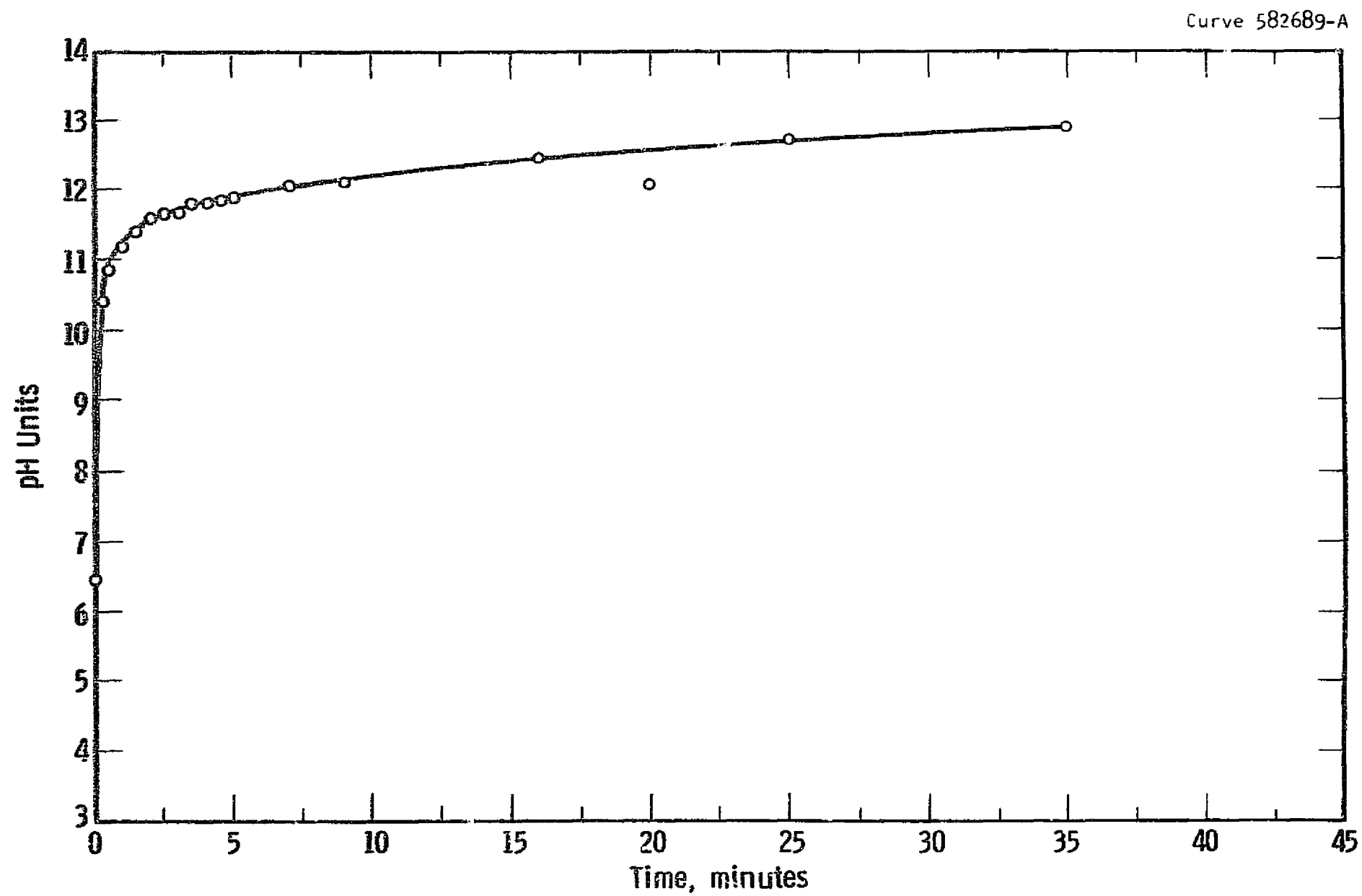


Fig. 25—Electrolyte diffusion time, 40% KOH, 26°C. PUDC 193 cellophane, ave. thickness 1 mil

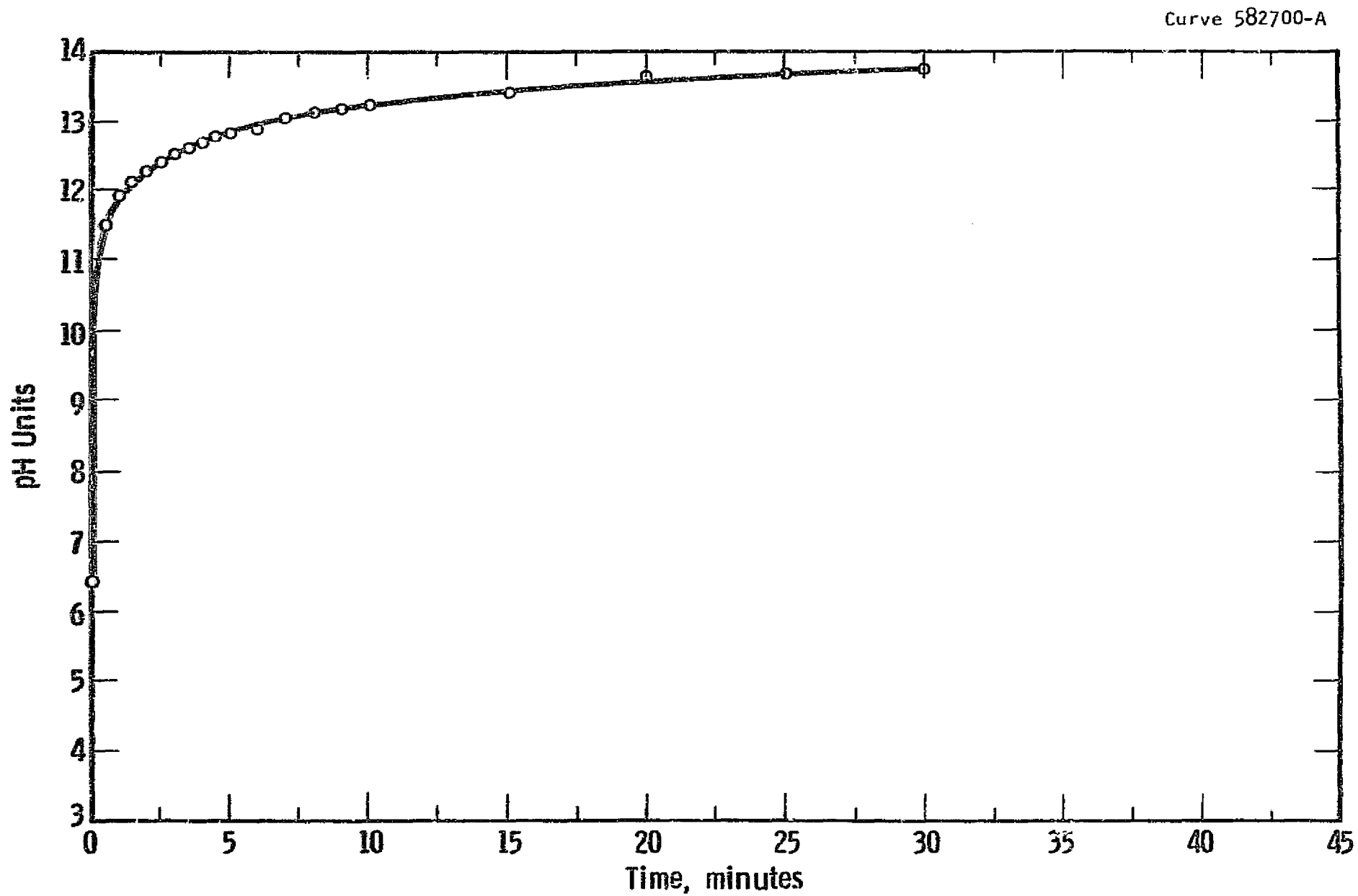


Fig. 26—Electrolyte diffusion time, 40% KOH, 26°C. Sample C58-4-3-8 extracted 30 min. in H₂O:
dioxane (25:75), ave. thickness 2.58 mils, Zeolon H : Polysulfone 20:15

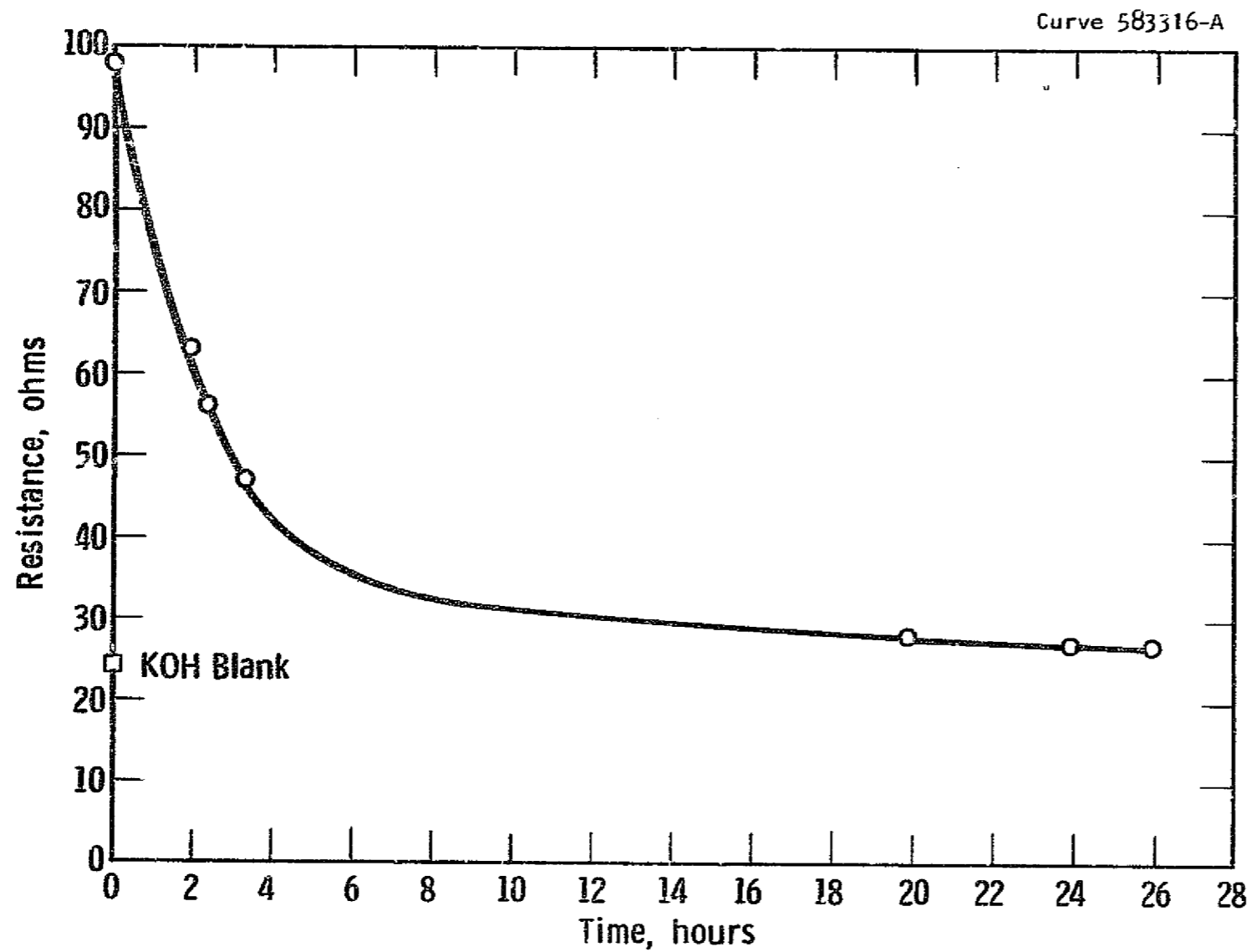


Fig. 27—Sample after 24 hours soak in 40% KOH. Decrease of resistance as a function of time of exposure to 40% KOH in bridge cell

Curve 587565-A

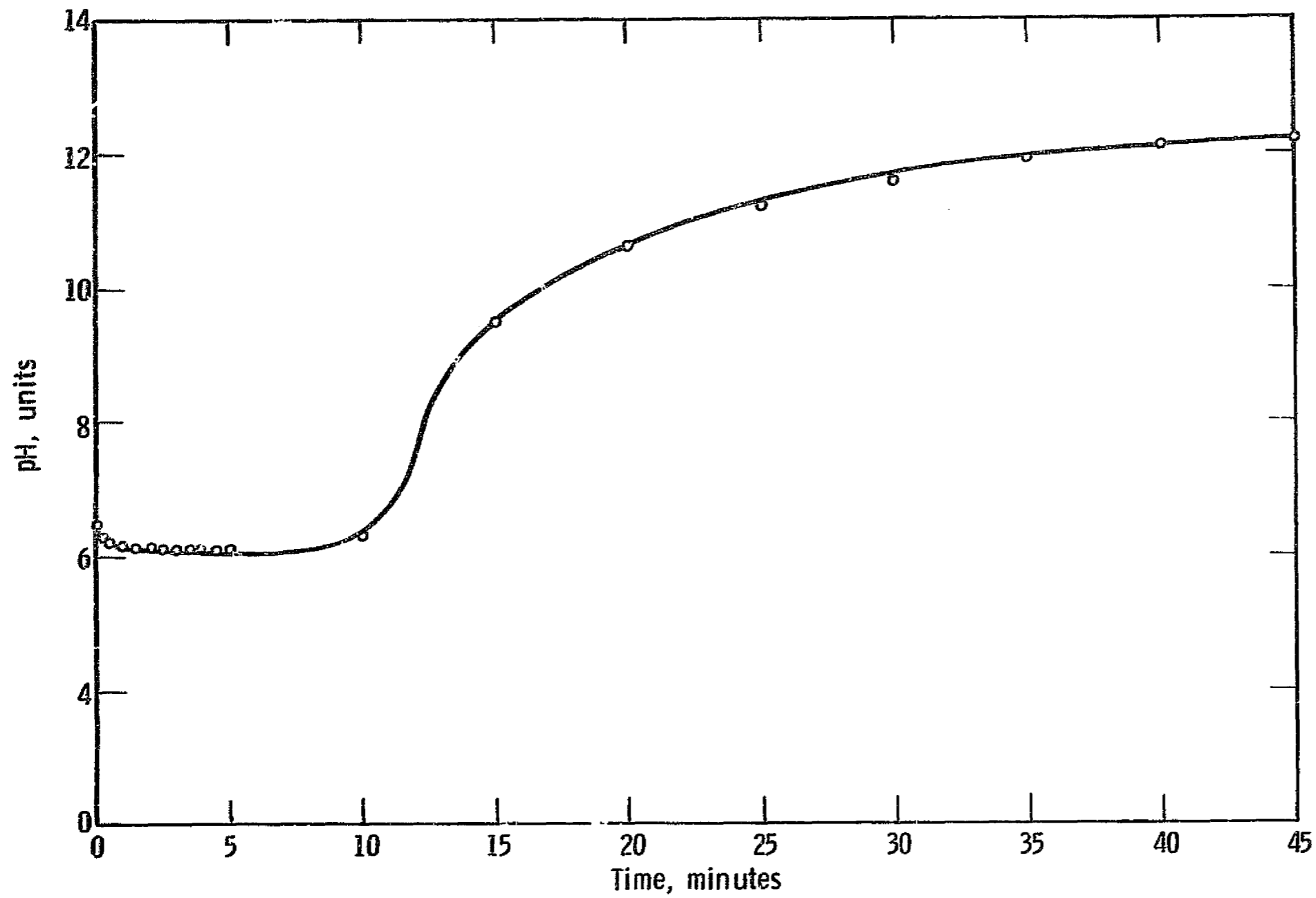


Fig. 28—Electrolyte diffusion time through Pellon composite