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ENGINEERING REPORT

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Delco-Remy

DIVISION OF GENERAL MOTORS, ANDERSON, INDIANA

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Project Nr. 8173

Task Nr. 817304-21

APPLIED RESEARCH INVESTIGATION OF SEALED SILVER-ZINC BATTERIES

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Sealed Silver Oxide-Zinc Battery Investigation

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FOREWORD

This report was prepared by Delco-Remy Division of General Motors Corporation, Anderson, Indiana, on Air Force Contract Nr. AF 33(657)-8943, under Task Nr. 817304-1 of Project Nr. 8173, "Investigation of Silver-Zinc Battery". The work was administered under the direction of Flight Accessories Laboratory, Wright Air Development Division; Mr. J. E. Cooper was task engineer for the laboratory.

The assistance of Dr. T. P. Dirkse, Professor of Chemistry, Calvin College, Grand Rapids, Michigan, as consultant on this project is greatly appreciated.

This report is being published and distributed prior to Air Force review. The publication of this report, therefore, does not constitute approval by the Air Force of the findings or conclusions contained herein. It is published for the exchange and stimulation of ideas.

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ABSTRACT

Cycle life data on cells containing varying ratios of ZnO to silver indicate that increasing the ratio of ZnO to silver tends to increase cycle life.

Separator overhang life tests are continuing after 500 cycles without failure.

Electrolyte quantity tests at this time are not conclusive in determining maximum cycle life. Additional work is to be done in this area.

Cells containing Dynel wrapped negatives do not show consistent cycle life, and on this test, do not deliver as many cycles as the control cells. Additional samples of Dynel will be utilized in new test cells.

Solubility curves have been obtained for ZnO and Ag_2O in NaOH, LiOH, and KOH.

Literature investigations concerning the use of electrolytes for silver-zinc electrodes other than strong bases are not promising.

Test cells utilizing CdO and double grids in the negative plate are still on cycle test. Some failures have occurred around 700 cycles, but no definite conclusions can be reached as yet.

Some evaluation tests for separators are under way and early sample materials have been received from both R.A.I. and the Viskking Corporation.

I. Introduction

The objective of this program is to provide additional design criteria for long life, light weight sealed secondary batteries for military aerospace application through the investigation of the silver oxide-zinc potassium hydroxide electrochemical system.

The specific items to be studied under this contract are:

A. Negative and Positive Plate Stiochiometry
B. Separator Overhang
C. Electrolyte Quantity
D. Dynel Wrap and New Polypor Films
E. NaOH and LiOH Studies
F. Insoluble Plate Materials
G. Conductive Matrices
H. Evaluation Tests for Separator Materials

This report covers the initial three month's work on these items.

The final data obtained from these studies will be utilized in the construction of test cells which will best meet the following specifications:

> 5000 continuous cycles at 27 ± 1.5 volts while operating in the temperature range 0°F to 100°F in vacuum of 10^{-5} mm Hg and in a zero gravity environment. A cycle is defined as 35 minutes discharge at 20 amperes followed by 85 minutes charge.

The two-hour cycle as defined above is used exclusively in this program, except for initial conditioning deep discharges.

II. Factual Data

A. Negative and Positive Plate Stoichiometry

Four groups of three 25 a.h. sealed cells were constructed with zinc-oxide negative active material employed in the following ratios to silver: 2:1, 1.5:1, 1:1, 0.75:1

These cells were activated in 45% KOH and cycled at 25% depth of discharge. A group is considered a failure when the one cell in the group fails.

Figure 1 shows the capacities obtained on the initial discharge of these four groups.

Figure 2 shows the end of discharge voltages for the indicated number of cycles obtained to date. The voltages are the average of three cells in each group.

It is immediately evident that decreasing the amount of ZnO below a 1:1 ratio is detrimental to both capacity and cycle life, and that increasing the ZnO ratio to silver increases the capacity and cycle life.

The cause of failure of these cells was the negative plate limiting the cell capacity, due to excessive washing of active material. Since the silver electrode capacity is not appreciably reduced during cell cycle life and is more than sufficient for the cell capacity during the 35 minute discharge, an additional increase in the ZnO to silver ratio of 4:1 will be studied by reducing the silver electrode capacity of the cell.

This will be accomplished by constructing cells of thinner positive plates and maintaining the standard thickness of the negative plate.

Six cells are under construction utilizing these plates. Twelve additional cells with 2% palladium coated silver particles in the positive plate are being constructed in the same manner. These cells will be cycle life tested at 25% depth of discharge on the two-hour cycle program.

B. Separator Overhang

In an effort to determine whether the zinc material growth can be controlled by varying separator overhang and plate area, the following twenty-four 25 a.h. sealed cells have been constructed, activated in 45% KOH, and placed on life-cycle test at 25% depth of discharge:

1. three cells with 1/8 inch separator overhang at the plate tops
2. three cells with 1/4 inch separator overhang at the plate tops
3. three cells with 1 inch separator overhang at the plate tops
4. three cells with 1/4 inch separator overhang around the perimeter of the positive plates using standard-size negatives
5. three cells with 1/2 inch separator overhang around the perimeter of the positive plates using standard-size negatives
6. three cells with 1/4 inch separator overhang around the perimeter of the negative plates using standard-size positives
7. three cells with 1/2 inch separator overhang around the perimeter of the negative plates using standard-size positives
8. three cells as controls, which utilize 1/8 inch separator overhang around the sides and bottoms of the plates, with 1 inch overhang at the tops of the plates.

A group is considered a failure when one cell in the group fails.

Figure 3 shows the end of discharge voltages at indicated cycles obtained for the first three groups of cells plus the control group.

Figure 4 shows the end of discharge voltages at indicated cycles obtained for groups 4 through 7.

C. Electrolyte Quantity

The required amount of electrolyte for cycling sealed silver-zinc cells has at times been questionable. Too much (flooded) electrolyte in a sealed cell has the tendency to increase cell internal pressure and cause premature washing of negative active material. Too little electrolyte can cause premature cell failure by increasing internal cell resistance.

This study is conducted to determine some parameters such as voltage, capacity, and cycle life dependent on amount of electrolyte required.

Three groups of three 25 a.h. sealed cells were activated with excess 45% KOH (i.e., 100 c.c.) and soaked for about a week. The excess electrolyte was drained from two groups. One group of three 25 a.h. sealed cells was activated with 75 c.c. and soaked. These were given initial discharges and placed on cycle life test.

Figure 5 shows the initial capacities obtained with the indicated electrolyte quantities. Group D was activated with 75 c.c. and not drained.

Figure 6 shows the end of discharge voltages at the indicated cycles obtained for these cells.

D. Dynel Wrap and New Polypor Films

The major cause of failure in silver-zinc cells undergoing this two-hour continuous cycle regime is due to the negative plate limiting cell capacity because of excessive washing of the active material. In an effort to prolong this washing effect, one to two layers of Dynel were used to wrap the negative plate prior to wrapping with regular separation.

Three groups of three sealed 25 a.h. cells, activated in 45% KOH, were constructed with one and two layers of Dynel (Webril 425) wrapped around the negative plate and placed on cycle life test at 25% depth of discharge. A control group with no Dynel negative wrap is included in this test.

Figure 7 shows the end of discharge voltages at the indicated cycles obtained. A group is considered a failure when one cell in the group fails. Table I shows the cycles obtained for each failing cell tested in the above four investigations (A through D).

E. NaOH and LiOH Electrolytes

In an effort to reduce the zinc washing and treeing and to reduce

silver penetration in the separators during cell operation, NaOH and LiOH are under investigation as possible replacements for KOH. Solubility studies have been experimentally conducted with Ag_2O and ZnO in various concentration ranges of NaOH and LiOH for comparison with the standard KOH electrolyte. Figure 8 shows the solubility range of Ag_2O in LiOH, NaOH and KOH at the indicated concentrations. Figure 9 shows the solubility range of ZnO in LiOH, NaOH and KOH at the indicated concentrations. The method of preparation used in preparing solutions of Ag_2O is as follows:

> Supersaturated solutions of Ag_2O were made up in various concentrations of NaOH, LiOH, and KOH by heating at 44°C for 3 days, the samples being shaken at intervals. The samples were then allowed to stand at room temperature for several days. Then the samples were filtered through a fine sintered glass filter, then neutralized to a methyl orange end point and titrated with .01 N KI to obtain the solubility data.
>
> Supersaturated solutions of ZnO were made in the same manner as the Ag_2O samples. The solubility data were obtained using standard zinc analysis [1].

F. Insoluble Plate Materials

The major cause of short cycle life of the silver-zinc cell is due to the solubility of the plate materials during charge or discharge in the electrolyte. Under the two-hour cycle regime specified, the rates employed are not considered high rates due to lack of recharge capability, so that weaker electrolytes might possibly be utilized if increased cycle life could be obtained at little or no cost to performance.

A theoretical study is under way to investigate different anions that might be compatible with the silver and zinc electrodes. To date, it has been found that two main problems are expected to arise from thermodynamic considerations:

1. The use of Ag with the electrolytes reviewed, such as salts of

strong acids, would prohibit cell operation on the divalent silver level, thus cutting the Faradaic capacity of the silver electrode in half;

2. The use of Zn with other classes of electrolytes reviewed is expected to result in a chemical displacement of metal or metaloid constituent in the electrolyte.

While the results of these thermodynamic studies have not been encouraging, it is planned to check out single electrode cycling behavior in several representative electrolytes of each class to determine whether the thermodynamic predictions will be borne out experimentally.

G. Conductive Matrices

In order to control the washing of the zinc active material, various amounts of CdO have been incorporated in the negative plate material for conductivity purposes by essentially providing an extension of the grid. Along with the CdO additions, a double grid has been utilized which completely surrounds the zinc active material to provide additional aid in suppressing the washing effect.

Four groups of three sealed 25 a.h. cells containing 20%, 10%, and 5% CdO additions in the negative mix were activated in 45% KOH and cycled at 25% depth of discharge.

Figure 10 shows the end of discharge voltages at the indicated cycles obtained.

Four additional groups of three sealed 25 a.h. cells containing 20%, 10%, and 5% CdO with double grids were activated in 45% KOH and cycled at 25% depth of discharge. Figure 11 shows the end of discharge voltage at the indicated cycles obtained. A group is considered a failure when one cell in the group fails. Failing cells are listed in Table 1.

H. Evaluation Tests for Separator Materials

In conjunction with the work being done by Radiation Applications

Incorporated and the Visking Company, screening tests for separator materials to be supplied by these companies during the course of this program are being developed. There are six main tests which will be used to determine the usability of membrane samples as separator material for use in the silver-zinc cell:

1. Conductivity in strong KOH solutions
2. Reactivity with Ag_2O and AgO in strong KOH solutions
3. Diffusion of KOH through the materials
4. Diffusion of zincate ions and the silver species through the materials
5. Deterioration in strong KOH solutions
6. Resistance to penetration by zinc dendrites.

To date six sample membrane materials have been received from R.A.I., and two sample membrane materials have been received from the Visking Company. The following screening tests have been performed on some of the samples received in the time prior to the publication of this report. In all cases, fibrous casing is used as a control membrane.

1. Conductivity in Strong KOH Solutions

Conductivity tests were run on all the sample membranes received. Five different sections of each sample membrane were tested so that an average resistance reading was obtained for each sample.

Figure 12 shows the plastic cell used in determining resistance. The sample membrane is securely clamped between the two cells with a 1/8 inch hole through the center of the adjacent sides. At each end of each cell is a cadmium electrode which provides the working current of 20 ma. Electrolyte is introduced through ports at the rear of the cell, immersing the electrodes and sample membrane. Two plastic tubes directly over the cells support the Hg/HgO reference electrode which are in turn connected to a potentiometer. Readings in millivolts are recorded with and without membranes and the resistance is calculated according to the following formula:

$$R = \frac{E_M - E_B}{I} \times \text{area} = \text{milliohms in}^2$$

where E_M = millivolts with membrane

E_B = millivolts of blank

I = current in amperes

area = in^2

Table 1 shows the resistances of the membrane samples and actual plateau voltages obtained on the fortieth cycle for the numbers of layers of separation used between the positive and negative plates in the three plate cell test. Figure 13 shows the group of three plate cells used to evaluate the sample membranes on cell cycle test.

2. Diffusion of KOH Through Membranes

Figure 14 illustrates the apparatus used for determining KOH diffusion through sample membranes. The plastic cell unit consists of two identical halves, each half containing entry ports for stirring and admission of electrolyte and reference electrodes.

The membrane to be tested is placed in the center block over the 1 inch diameter orifice. The unit is securely clamped in place forming a tight seal around the perimeter of the membrane.

Distilled water is placed in the left-hand side of the cell, the cell being mounted on a magnetic stirring unit. The Calomel and glass electrodes are inserted as shown. Electrolyte is added to the right-hand side of the cell, such that the 1 inch diameter orifice covered by the membrane is completely covered. pH readings are recorded at 5 minute intervals for the first 20 minutes, then every 10 minutes for the remaining 70 minutes. The diffusion rate is expressed in terms of moles/in^2 in unit of time (minute) by the following equation:

$$\frac{\Delta M}{\Delta t} = \frac{\Delta C}{\Delta t} \times \frac{V}{A}$$

where M = mass change
t = time in minutes
V = volume of chamber (liters)
A = area of 1 inch diameter orifice
C = moles/liter

Figures 15, 16 and 17 show the change in KOH concentration with time for fibrous sausage casing, the 2.1H and 2.1L polyethylenes. The data of these curves result in mass transfer coefficients of 4.04×10^{-3}, 2.45×10^{-3}, and 1.92×10^{-3} moles/in^2-min. for F.S.C., R.A.I. 2-1H, and R.A.I. 2-1L, respectively, with the thickness reduced to a common value of one mil.

3. Diffusion of Zincate Ions Through Sample Membranes

The diffusion apparatus in this test is similar to that used to determine KOH diffusion as illustrated in Figure 14. The present test utilizes a potentiometric method, based on the fact that the electrode potential of the zinc-zincate ion couple at constant hydroxyl ion concentration varies by 0.0295 volts for every ten-fold concentration of the zincate ion. This is especially true in strongly alkaline solutions (45% KOH) where the dissolution of zinc oxide would have little effect on the hydroxyl ion concentration.

In actual measurement a sample membrane is soaked in distilled water for a time. It is then inserted in the center of the cell, covering a 2.33 in^2 orifice, and the two half-cell sections are securely clamped in place. The cell assembly is mounted on a magnetic stirring unit and the zincate free KOH is added to one side with the stirring bar in operation. A Hildebrand half cell for the Hg/HgO reference electrode and the amalgamated zinc indicator electrode are inserted in the cell. The potentials are measured on a Sargent Recorder. Diffusion time is measured from the time at which the recorder begins its downward trend. A diffusion of approximately 115 minutes is used. The diffusion constant is calculated from the

following equation:

$$K \text{ (moles/in}^2 \text{ in time, minutes)} = \frac{C_1 - C_2}{T \times A}$$

where C_1 = initial concentration of zincate
C_2 = final concentration of zincate
T = time
A = area of orifice

Figures 18 through 23 show the change in concentration of the zincate ion with time for the various test membranes with fibrous casing as the control.

III. Summary

The cycle life data obtained on cells under the plate stoichiometry study appears to indicate that a design change of the cells operating on the continuous two-hour cycle regime would be beneficial. This change would utilize thin positive plates and thick negative plates, utilizing something more than a 2:1 ratio of zinc to silver, based upon the theoretical silver a.h. capacity in the same cell package size. Investigation of higher than 2:1 ratios is under way.

Tests involving conductive matrices, separator overhang, Dynel negative plate wrap, and electrolyte quantity are not complete. Parameters such as voltage and cycle life are still to be determined.

In the solubility tests of Ag_2O in the several electrolytes, Ag_2O is more soluble in the higher NaOH concentration range compared to KOH. The Ag_2O is much more soluble in LiOH than KOH in the range of LiOH concentrations possible. Some cell tests will be conducted with LiOH and NaOH as electrolytes and performance characteristics will be compared with KOH-filled cells.

In the theoretical study of the possible use of electrolytes which would render both plate materials insoluble, thermodynamic calculations which describe the likelihood of achieving such electrolytes are not encouraging. Nevertheless, representative experimental data will be obtained for electrolytes of various classes to determine whether reaction kinetics involved might not override the thermodynamics and render such electrolytes possible of exploitation.

Several of the screening tests for separator membranes are under way. The test for Ag_2O diffusion through membranes is still under development, and it is expected that this test will be operational shortly. With respect to the screening tests outlined in this report, it is understood that as additional familiarity with new separators is acquired, new improved tests may result and older ones be abandoned.

Considerable data on separator membranes supplied by R.A.I. and Visking will be available in the next few months as the samples are furnished periodically.

IV. Bibliography

(1) Flescha, H., and Abdine, H., "Chemist-Analyst," Vol. 45, No. 3, p. 58-61 (1956)

(2) Amlie, R. F., and Rüetschi, P., "J. Electrochem. Soc.," Vol. 108, No. 9, p.813-822 (1961)

TABLE 1

CYCLES OBTAINED BY FAILED CELLS USED IN INVESTIGATIONS

OUTLINED IN PARAGRAPH A, B, C, D, G

	Cells	Group	Neg. to Pos. Weight Ratio	Cycles
A. Plate Stoichiometry	1	A	0.75/1	72
	2	A	0.75/1	72
	3	A	0.75/1	72
	4	B	1:1	240
	5	B	1:1	248
	6	B	1:1	288
	7	C	1.5:1	723
B. Separator Overhang Test		no failures		
C. Electrolyte Quantity	1	A		860
	1	C		48
	1	D		872
D. Dynel Wrapped Negatives	1	A		644
	2	A		680
	4	B		512
	5	B		584
	6	B		656
	7	C		352
	8	C		632
G. Conductive Matrices				
Single grid	1	A		668
Double grid	1	B		740

TABLE 2

Resistance of sample membranes in 45% KOH and related plateau voltages at 40 cycles with the indicated layers of membranes between the positive and negative plate

Company	Membrane	Resistance in milliohms in^2 Avg.	Dev.	Plateau Voltages Layers 1	2	3	4
RAI	2.1H (low density polyethylene, high graft)	42	± 6.3	1.49	1.47	1.45	1.45
RAI	2.1L (low density polyethylene, low graft)	91.9	± 22.4	1.46	1.41	1.44	1.42
RAI	2.3HX (low density polyethylene, high graft, crosslinked)	59.4	± 7.0	1.51	1.50	1.48	1.47
RAI	4.1H (high density polyethylene, high graft)	238.0	± 34.7	1.48	1.47	1.45	1.43
RAI	4.3HX (high density polyethylene, high graft, crosslinked)	168.6	± 22.6	1.46	1.42	1.42	1.45
RAI	5.1H (TFE Teflon, High graft)	68.5	± 6.6	1.49	1.51	1.51	1.48
Visking	2 C (RPS Fibrous casing)	29.5	± 1.2	1.52	1.51	1.48	1.48
Visking	8 A (High molecular weight casing)	27.1	± 1.7	1.52	1.51	1.50	1.49
Visking	Fibrous Casing (control)	30.5	± 3.2	1.49	1.51	1.50	1.49

TABLE 3

DIFFUSION OF KOH THROUGH MEMBRANES IN 45% KOH

Sample	Mass Transfer Coefficient $\frac{\text{moles KOH}}{\text{min.-in}^2}$	Thickness mils	Adjusted * Mass Transfer Coefficient $\frac{\text{moles KOH}}{\text{min.-in}^2}$
F.S.C.	0.792×10^{-3}	5.1	4.04×10^{-3}
R.A.I. 2-1H	1.53×10^{-3}	1.6	2.45×10^{-3}
R.A.I. 2-1L	1.28×10^{-3}	1.5	1.92×10^{-3}

* Adjusted Mass Transfer Coefficient

The mass transfer coefficients obtained directly from experimental data were adjusted to one mil thickness on the assumption that the diffusion should be inversely proportional to the thickness.

A = average voltage of three cells with 0.75:1 active material ratio

B = average voltage of three cells with 1:1 active material ratio

C = average voltage of three cells with 1.5 :1 active material ratio

D = average voltage of three cells (controls) with 2:1 active material ratio.

All cells activated in 45% KOH, cycling at 25% depth of discharge, at 80°F.

When one cell in a group fails, this is considered a group failure.

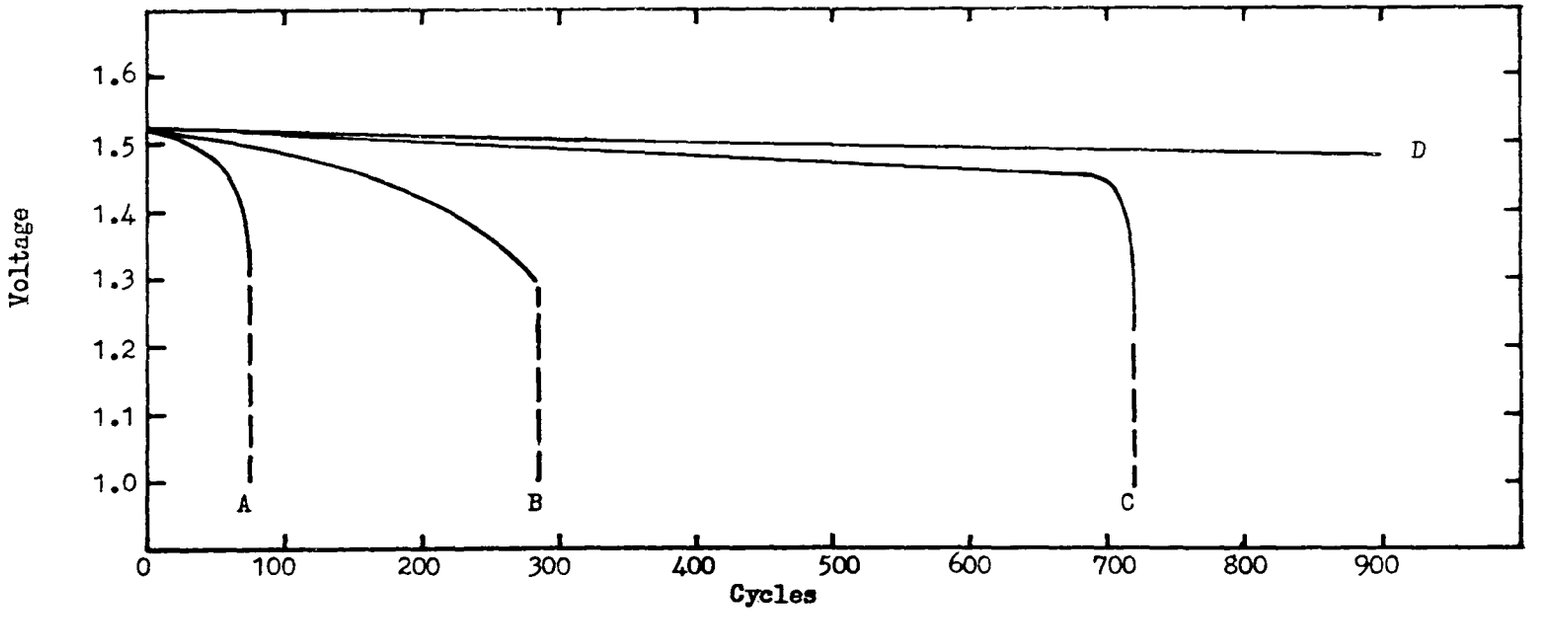

FIGURE 2 End of Discharge Voltages of Cells in Stoichiometry Study

A = average voltages of three cells containing 1" overhang separators

B = average voltages of three cells containing ½" overhang separators

C = average voltages of three cells containing 1/8" overhang separators

D = average voltages of three cells as controls.

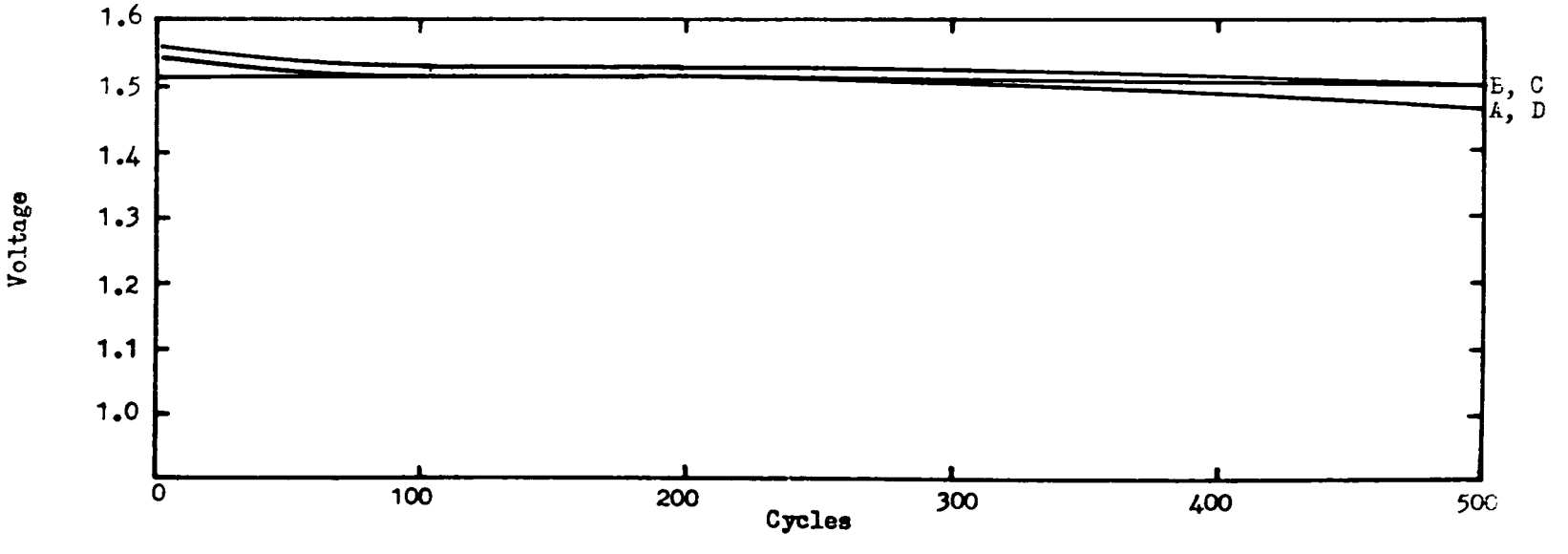

FIGURE 3 End of Discharge Voltages of Cells Containing Separator Overhang Variations

A = average voltages of three cells containing $\frac{1}{4}$" overhang around the perimeter of positive plates using standard negatives.

B = average voltages of three cells containing $\frac{1}{2}$" overhang around the perimeter of positive plates using standard negatives.

C = average voltages of three cells containing $\frac{1}{4}$" overhang around the perimeter of negative plates using standard positives.

D = average voltages of three cells containing $\frac{1}{2}$" overhang around the perimeter of negative plates using standard positives.

All cells cycled to 25% depth of discharge at 80°F.

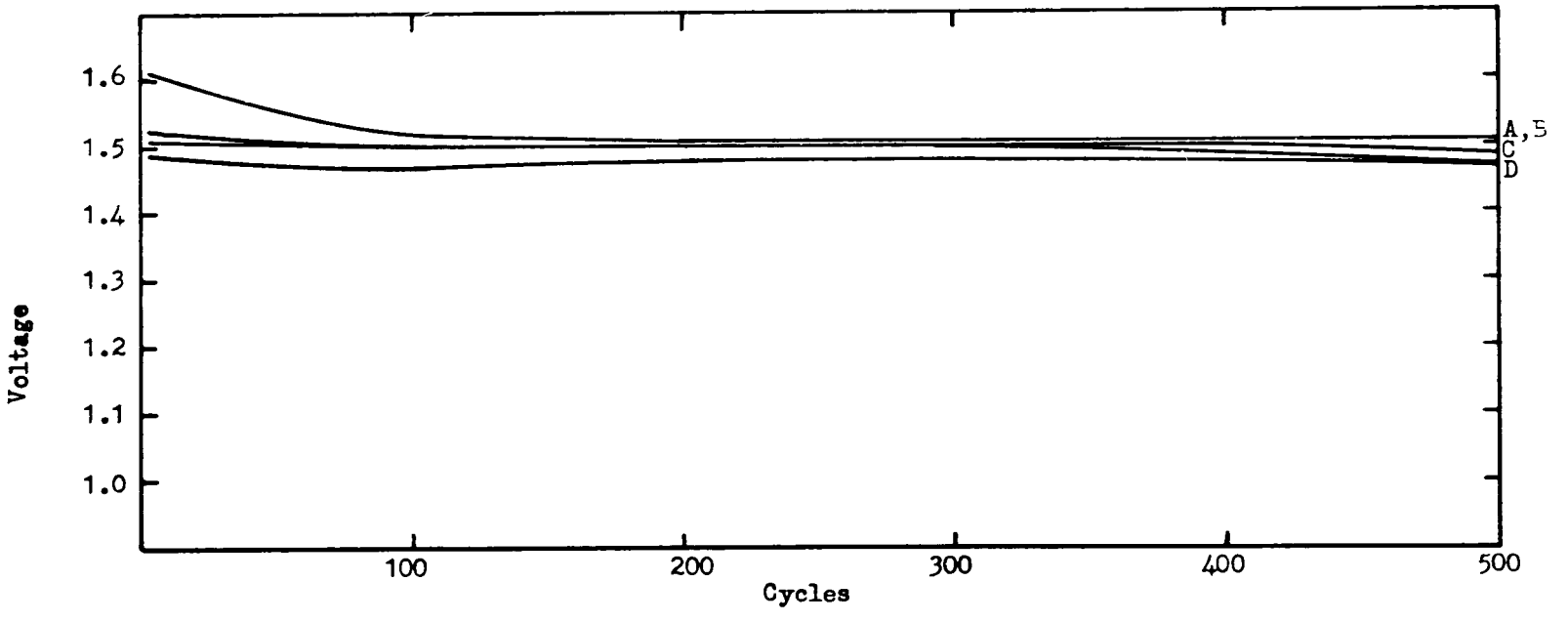

FIGURE 4 End of Discharge Voltages of Cells Containing Various Plate Areas

A = average capacity for three cells filled with 70 c.c. of 45% KOH
B = average capacity for three cells filled with 100 c.c. of 45% KOH
C = average capacity for three cells filled with 65 c.c. of 45% KOH
D = average capacity for three cells filled with 75 c.c. of 45% KOH

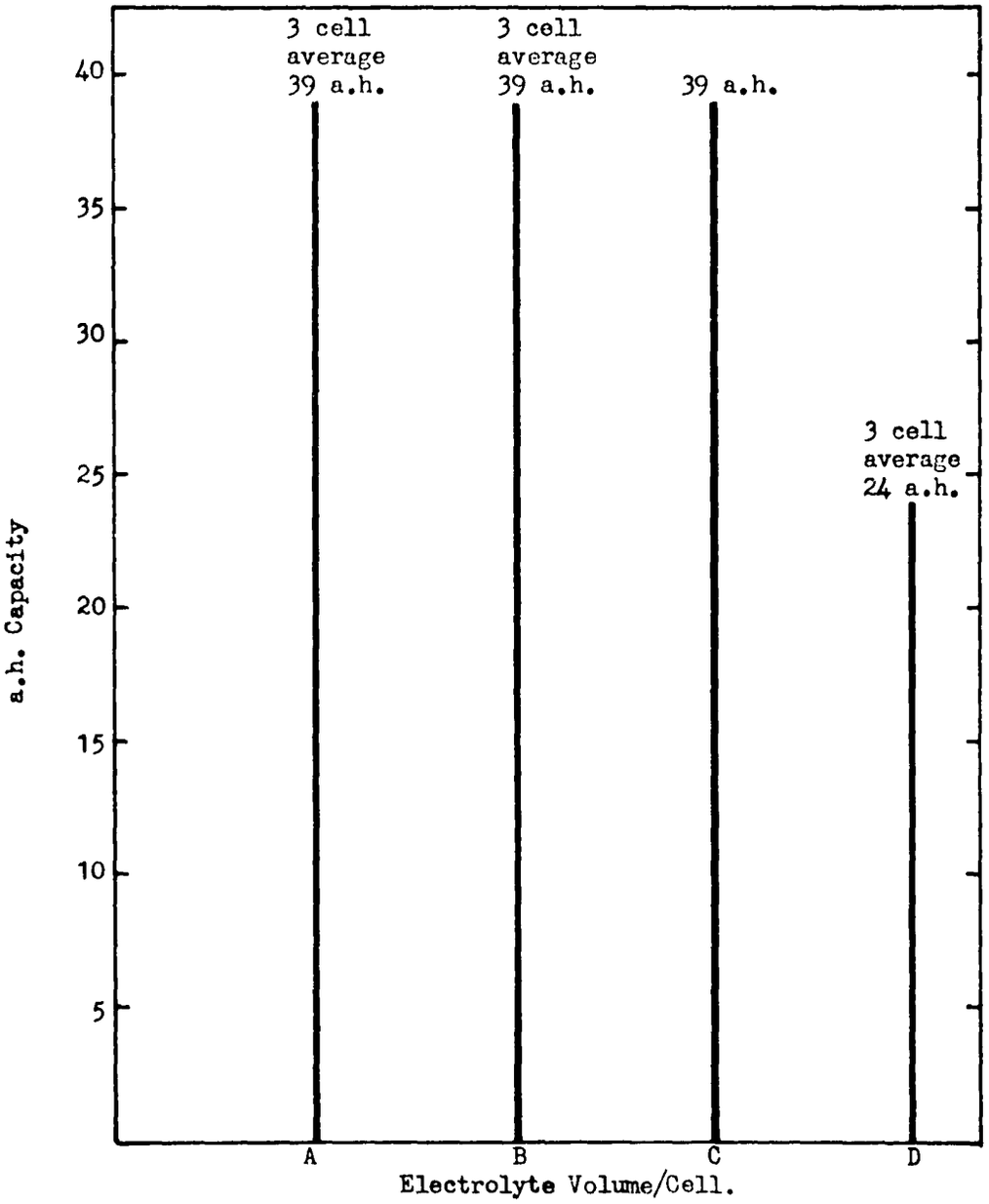

FIGURE 5 Initial Capacities of Cells in Electrolyte Volume Test

A = average voltage of three cells containing 70 c.c. of 45% KOH

B = average voltage of three cells containing 100 c.c. of 45% KOH

C = average voltage of three cells containing 65 c.c. of 45% KOH

D = average voltage of three cells containing 75 c.c. of 45% KOH

All cells were cycled to 25% depth of discharge at 80°F.

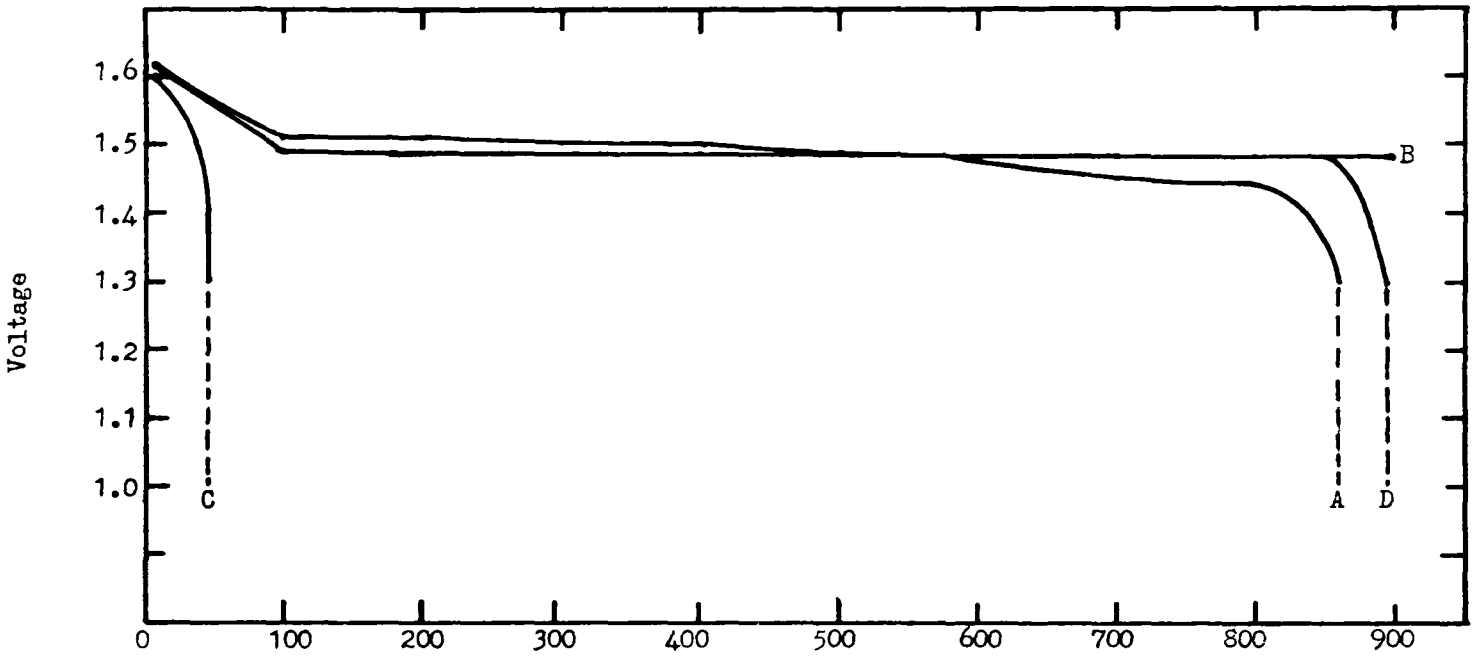

FIGURE 6 End of Discharge Voltages of Cells Containing Varying Amounts of Electrolyte

A = average voltage of three cells containing two layers of Dynel
B = average voltage of three cells containing one layer of Dynel
C = average voltage of three cells containing two layers of Dynel
D = average voltage of control cells.

All cells cycled to 25% depth of discharge at 80°F.

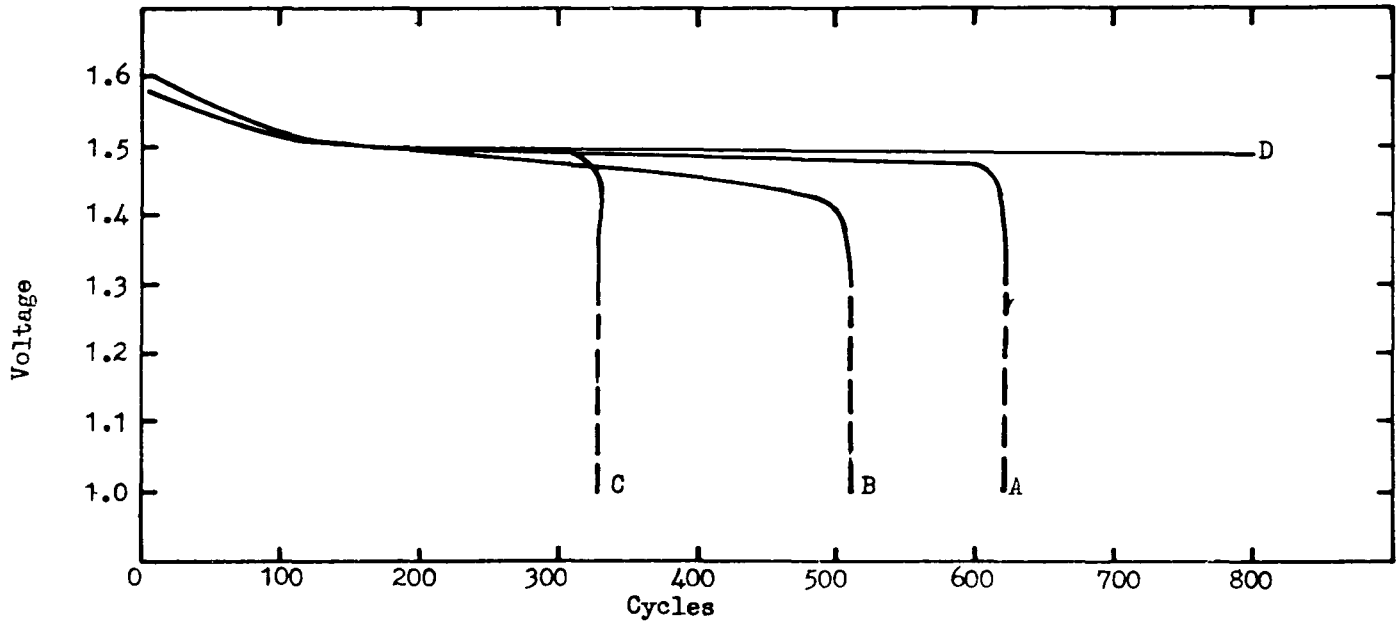

FIGURE 7 End of Discharge Voltages of Cells Containing Dynel Wrapped Negatives

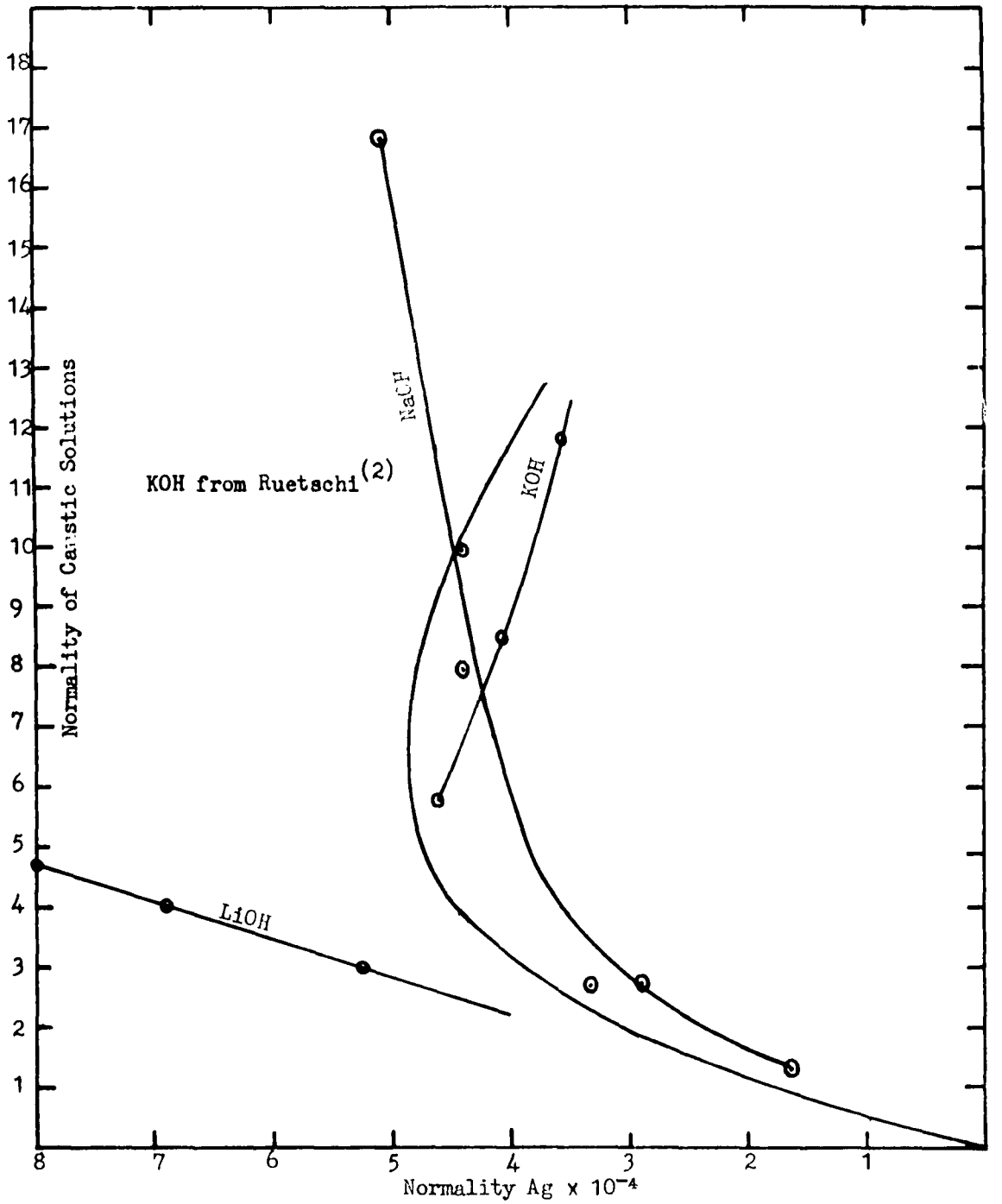

FIGURE 8 Solubility Range of Ag_2O in LiOH, NaOH, and KOH

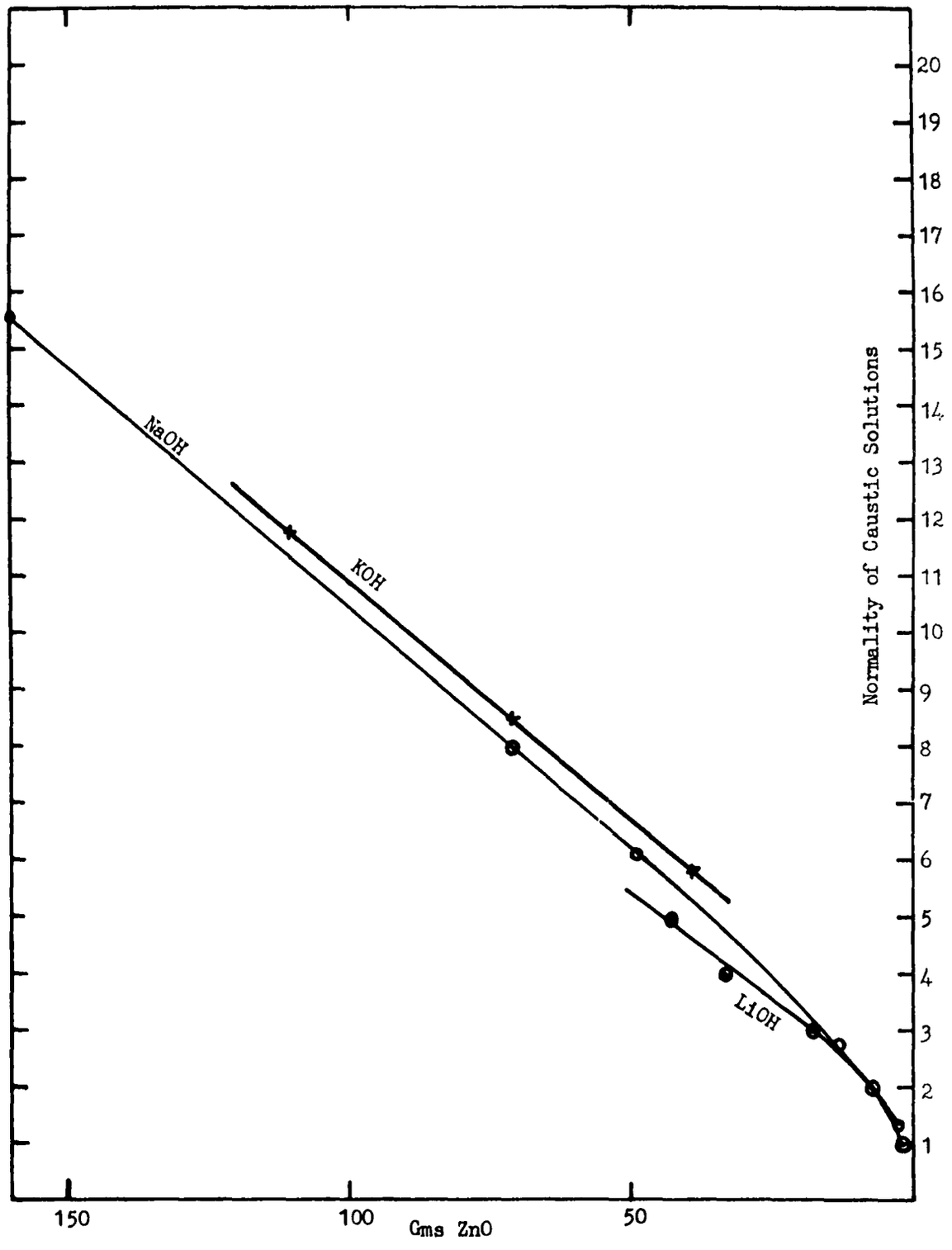

FIGURE 9 Solubility Range of ZnO in LiOH, NaOH, and KOH

A = voltage of three cells containing 20% CdO in negative plate

B = voltage of three cells containing 10% CdO in negative plate

C = voltage of three cells containing 5% CdO in negative plate

D = voltage of three control cells

All cells cycled at 25% depth of discharge at 80°F.

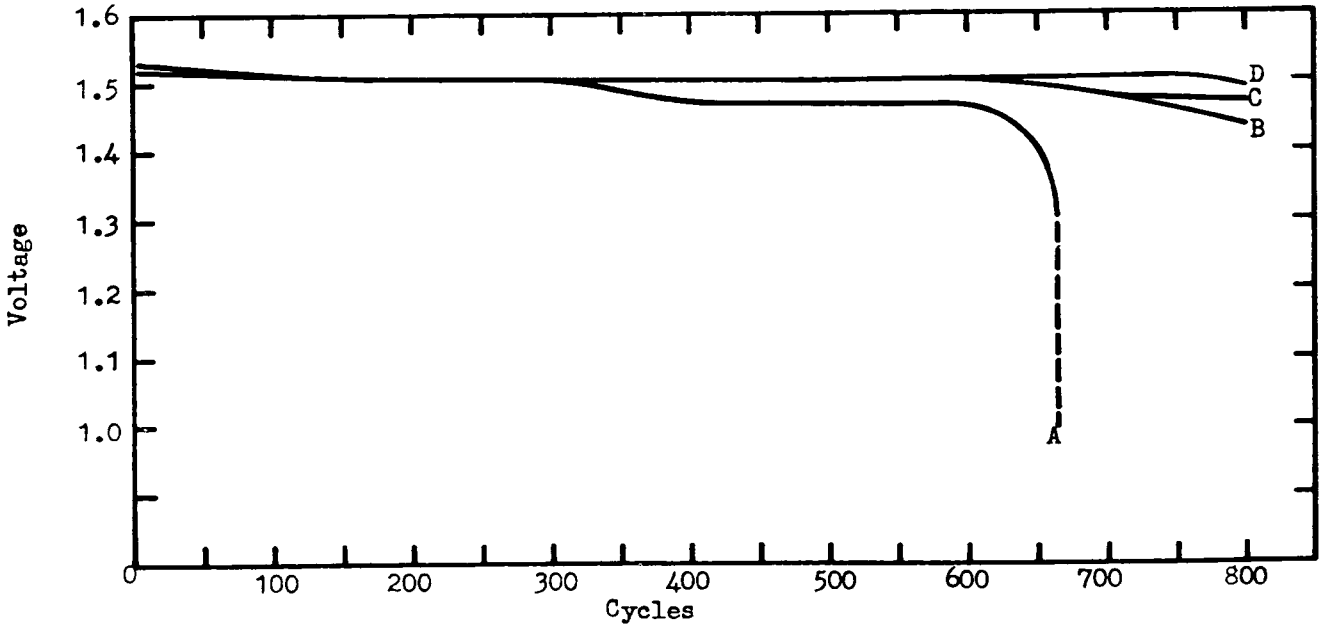

FIGURE 10 End of Discharge Voltages of Cells Containing CdO in Negative Material

A = voltage of three cells containing 20% CdO in double grid negative plate

B = voltage of three cells containing 10% CdO in double grid negative plate

C = voltage of three cells containing 5% CdO in double grid negative plate

D = voltage of three controls

All cells cycled at 25% depth of discharge at 80° F.

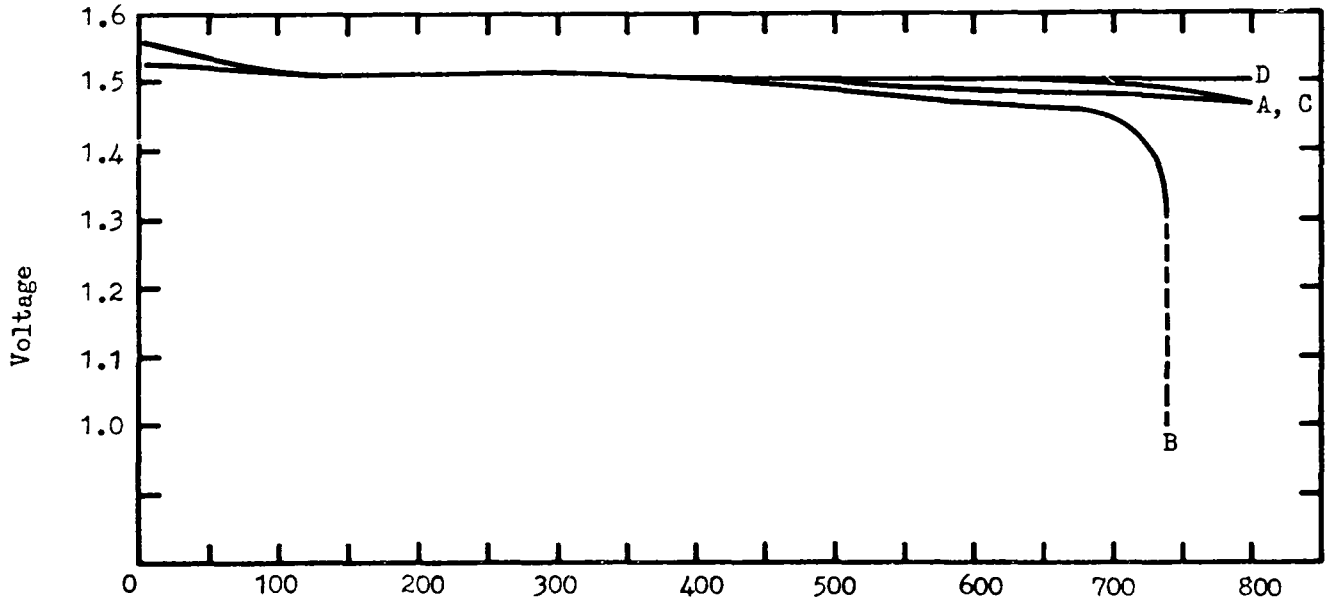

FIGURE 11 End of Discharge Voltages of Cells Containing CdO in Double Grid Negatives

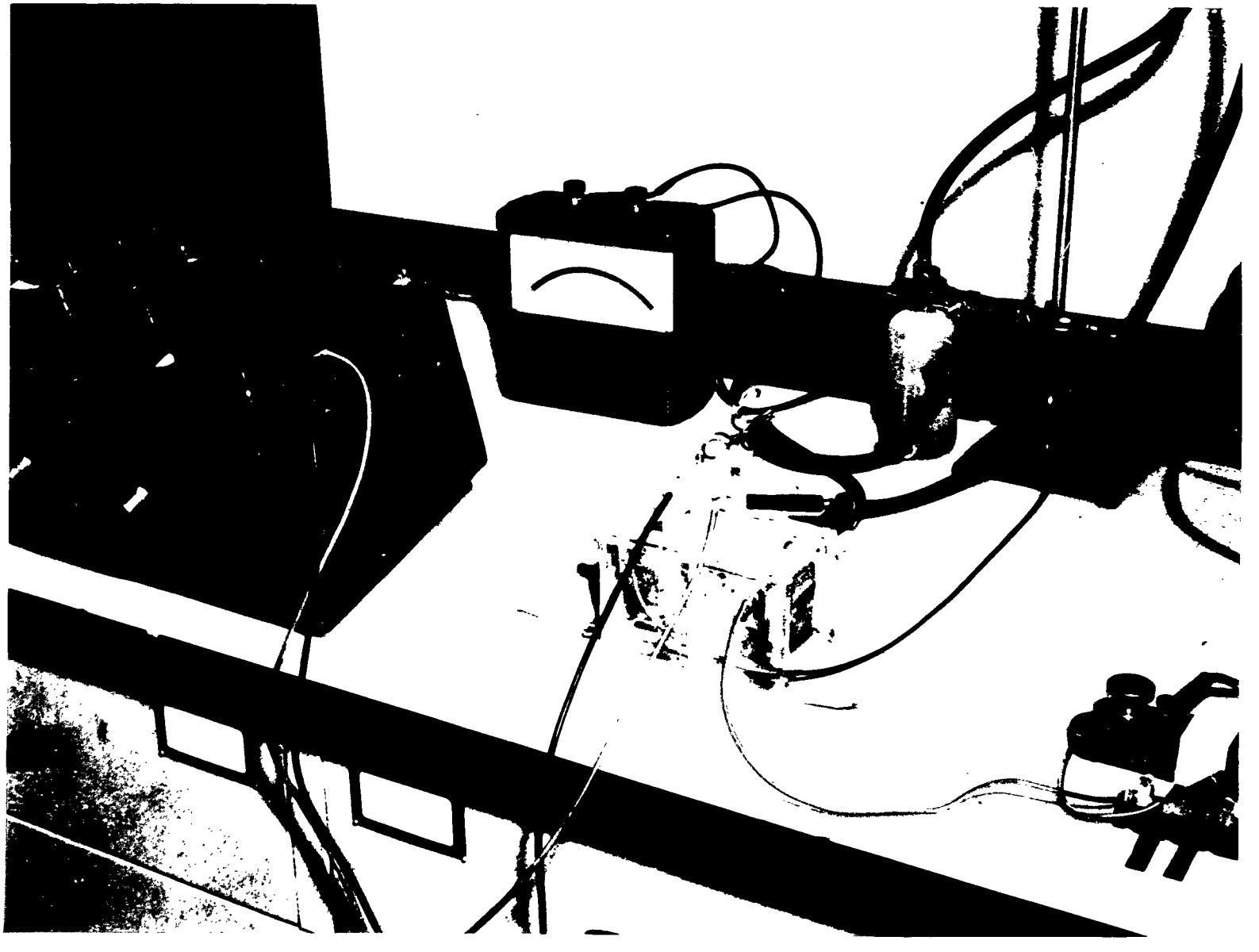

FIGURE 12 Conductivity Cell

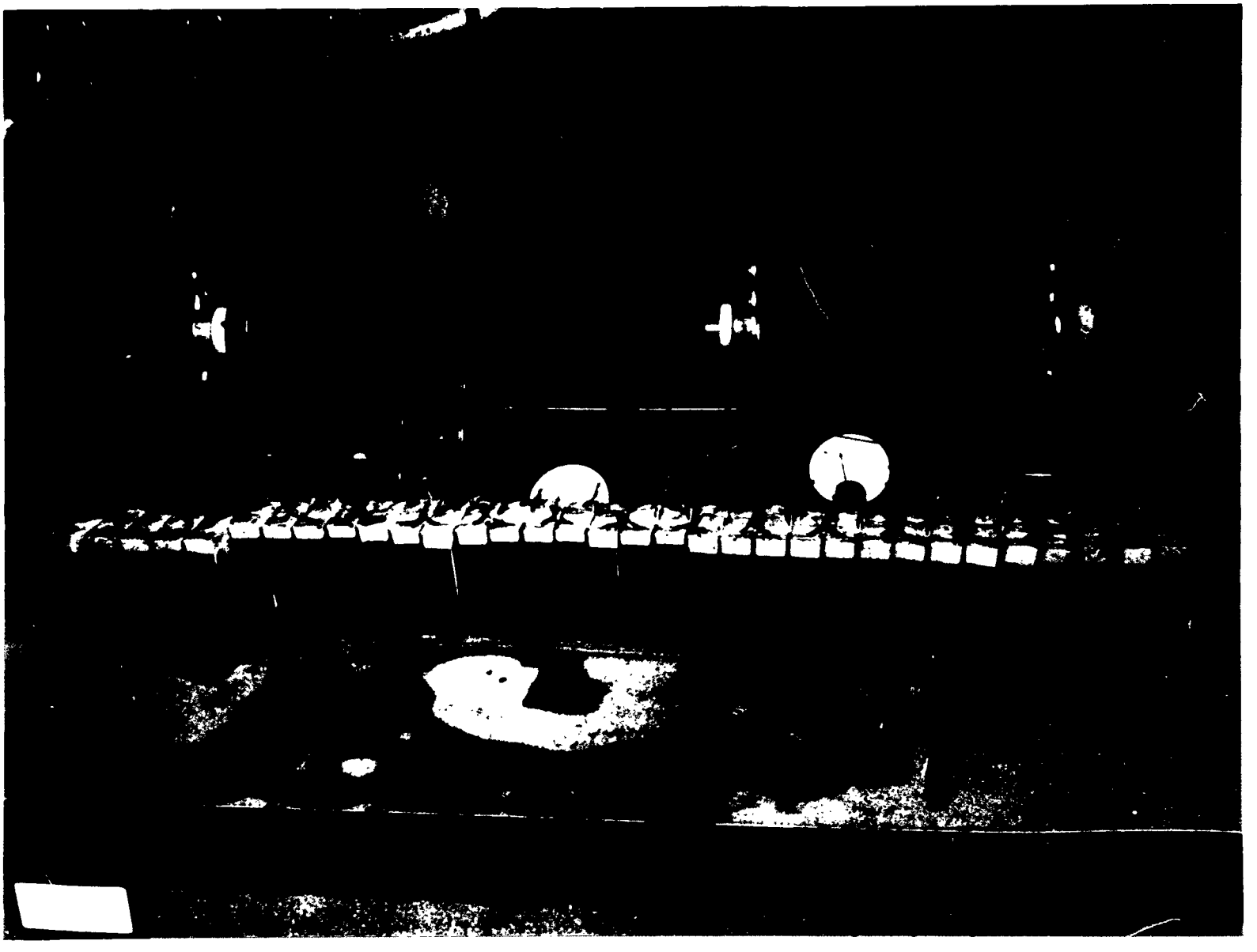

FIGURE 13 Three-Plate Cell Separator Cycle Test

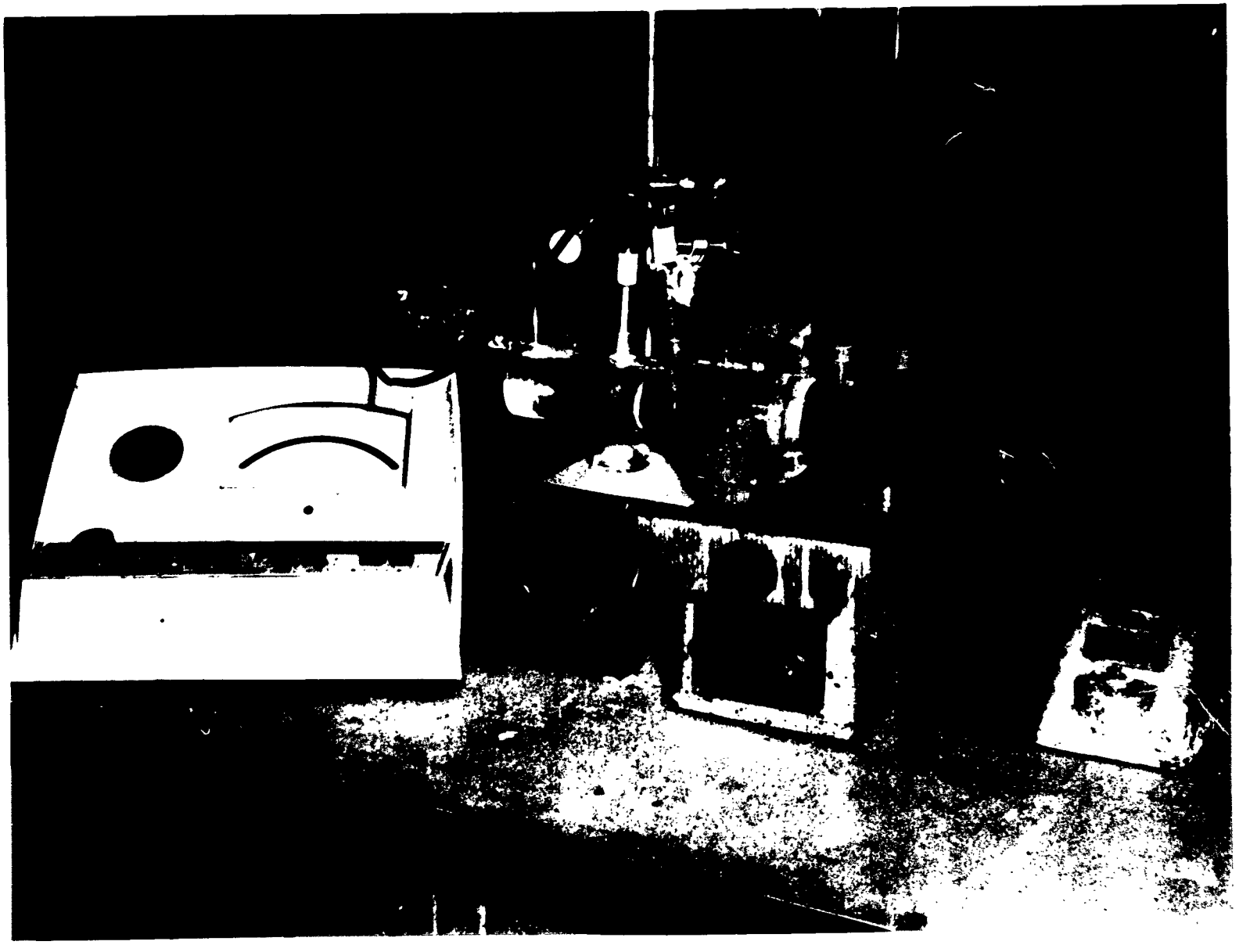

FIGURE 14 Cell Used for Determining KOH Diffusion Through Sample Membranes

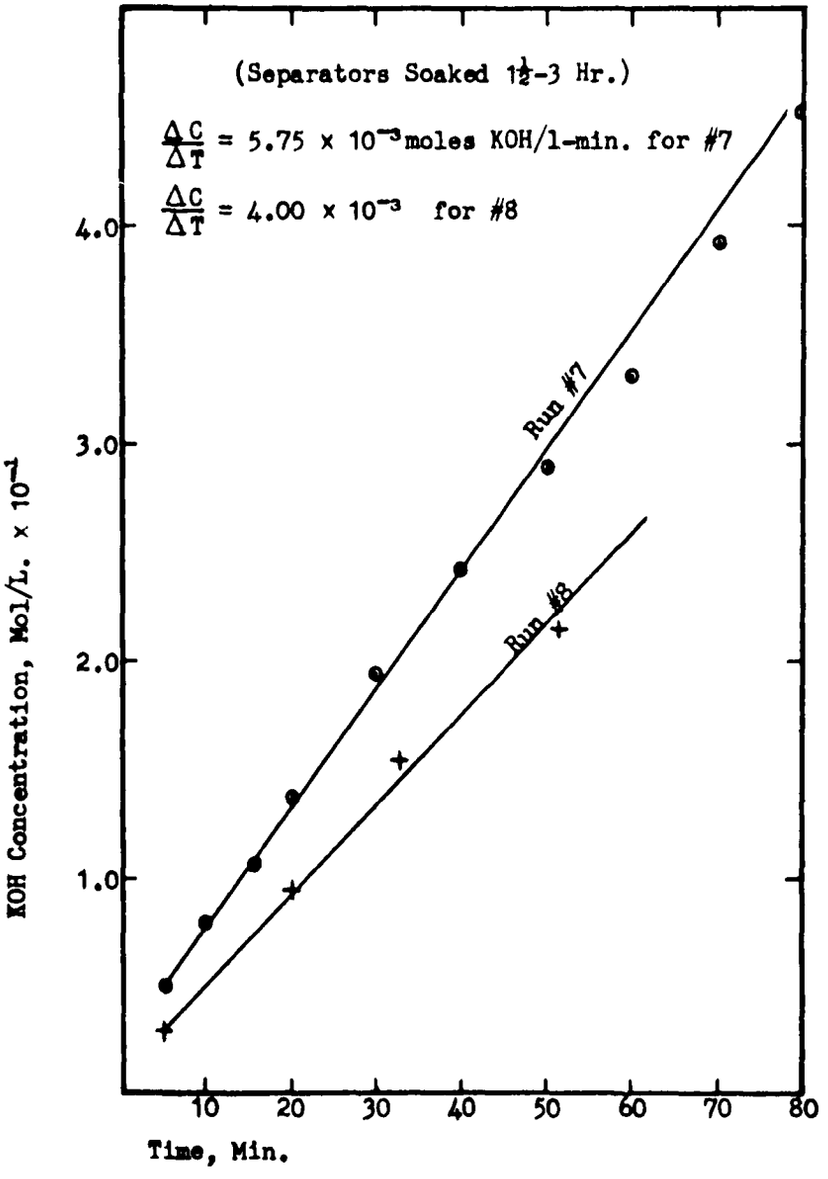

FIGURE 15 Diffusion of KOH Through R.A.I. 2-1L in 45% KOH

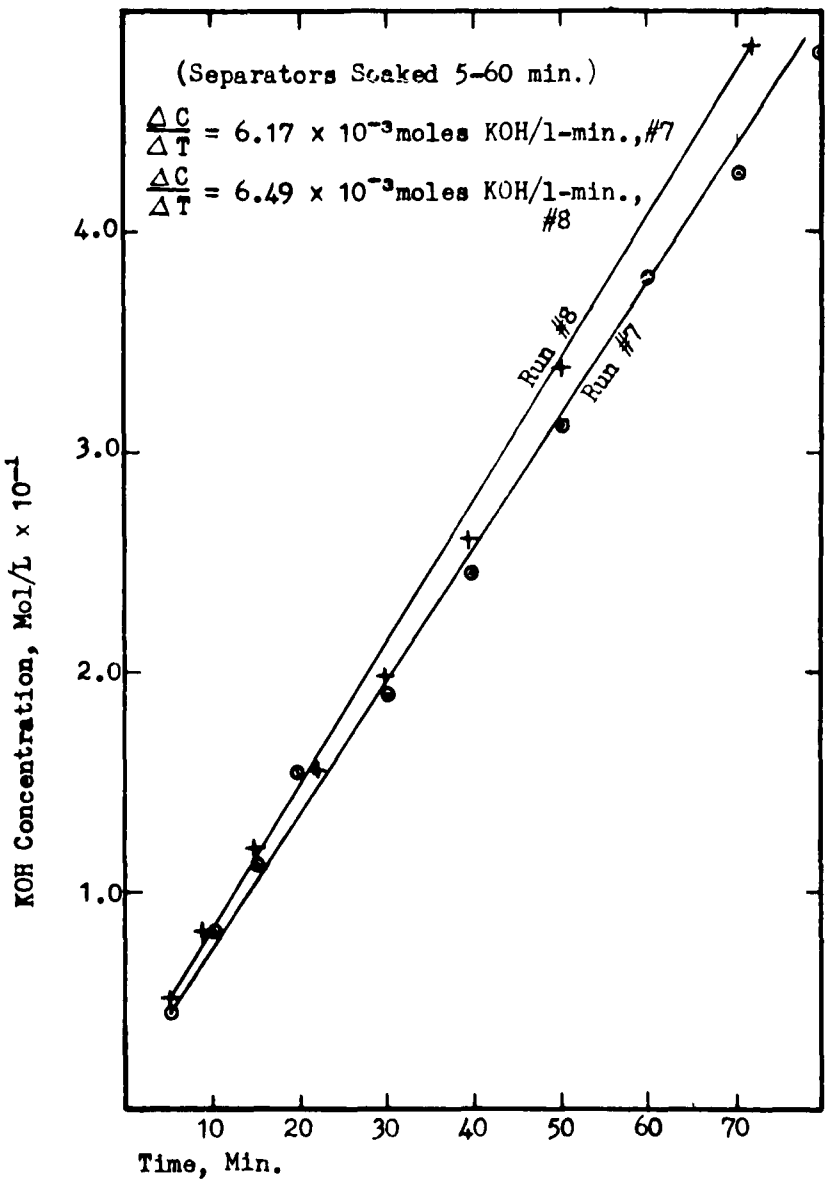

FIGURE 16 Diffusion of KOH Through R.A.I. 2-1H in 45% KOH

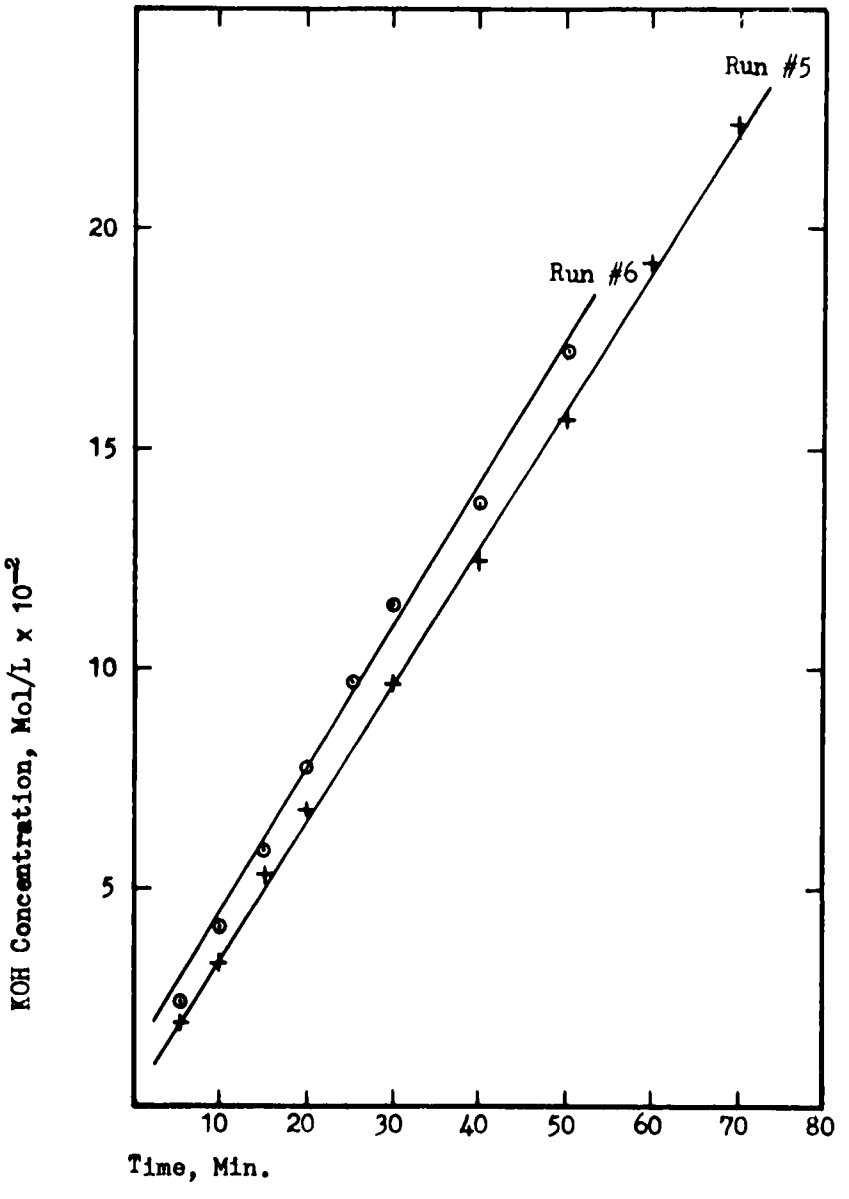

FIGURE 17 Diffusion of KOH Through F.S.C. in 45% KOH

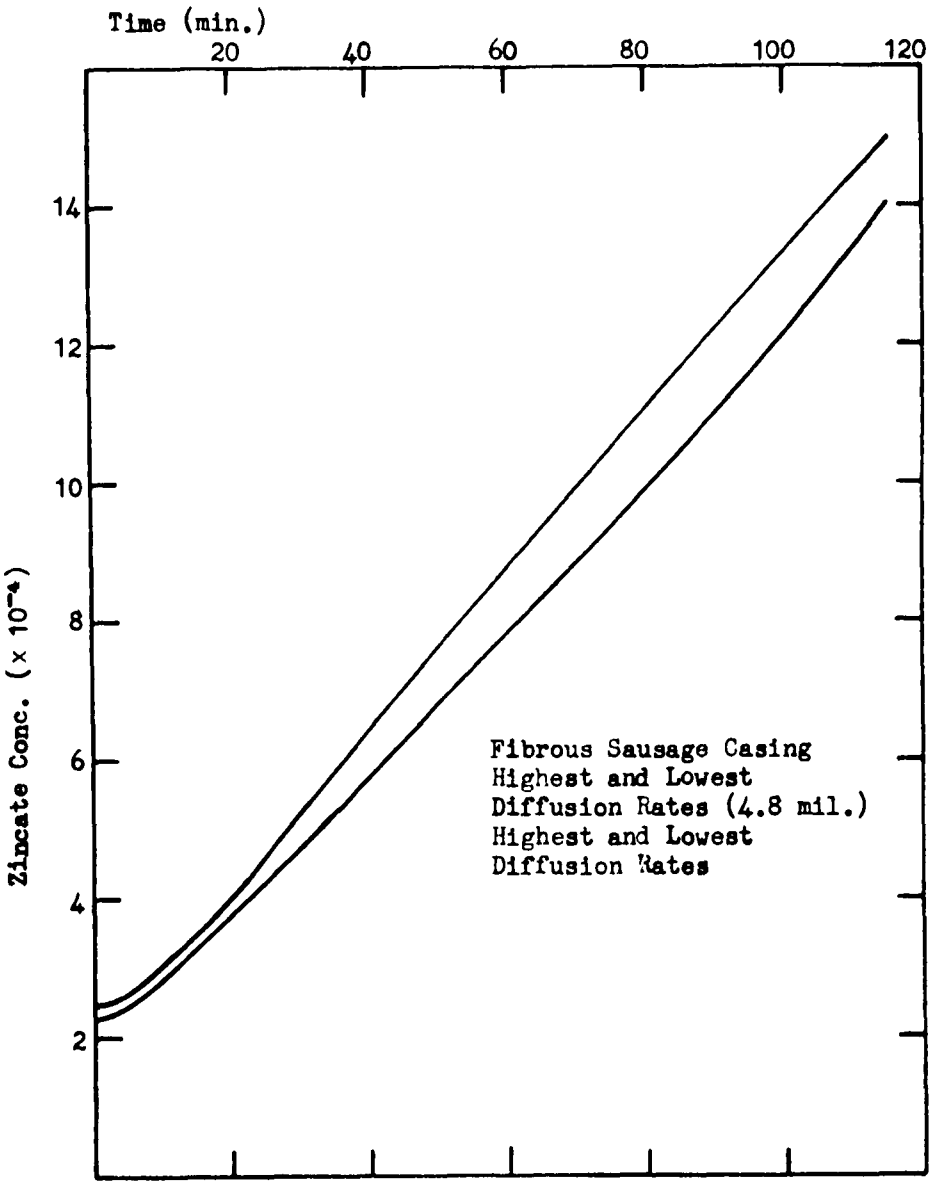

FIGURE 18 Zincate Concentration in 45% KOH by Diffusion Through Separator Materials

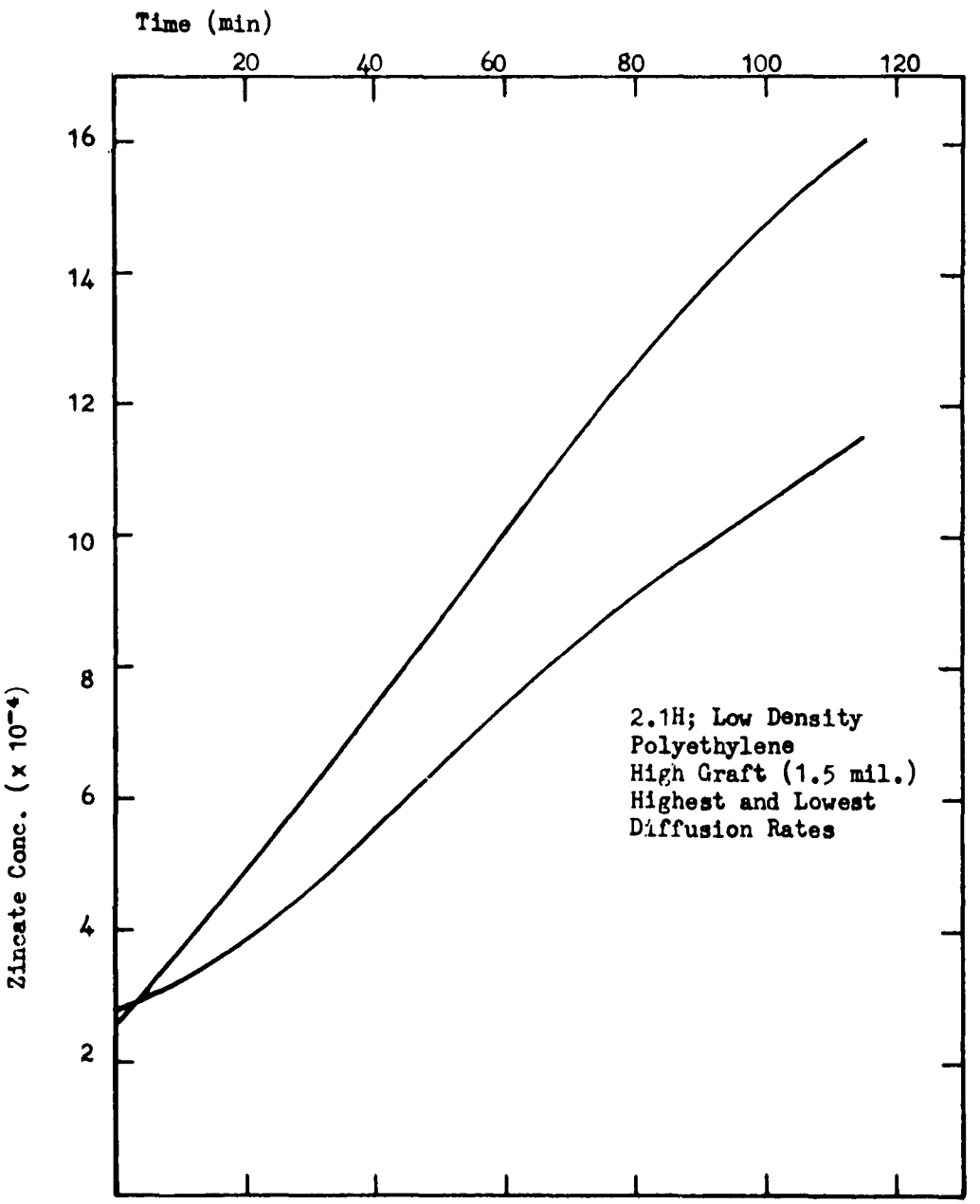

FIGURE 19 Zincate Concentration in 45% KOH by Diffusion Through Separator Materials

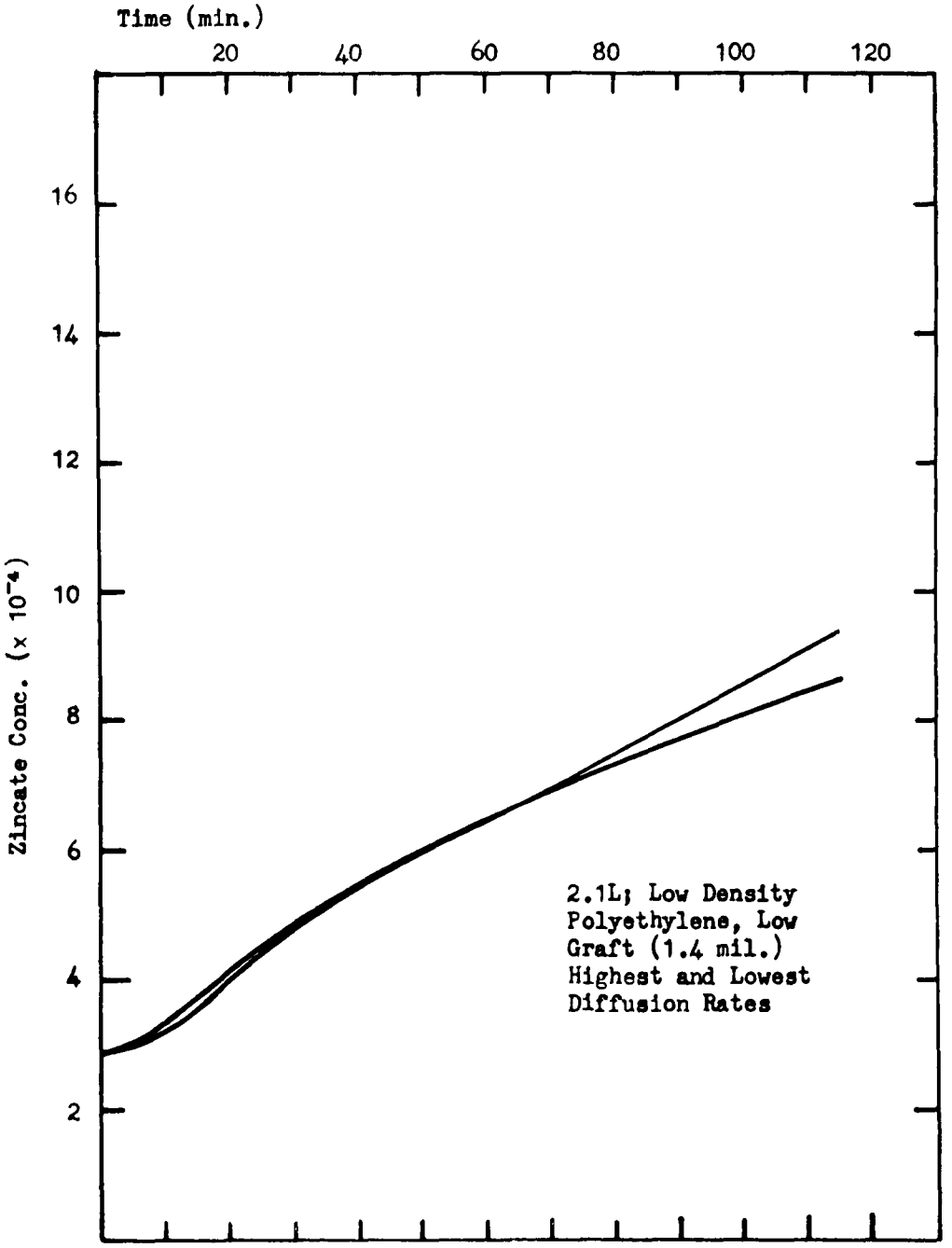

FIGURE 20 Zincate Concentration in 45% KOH by Diffusion Through Separator Materials

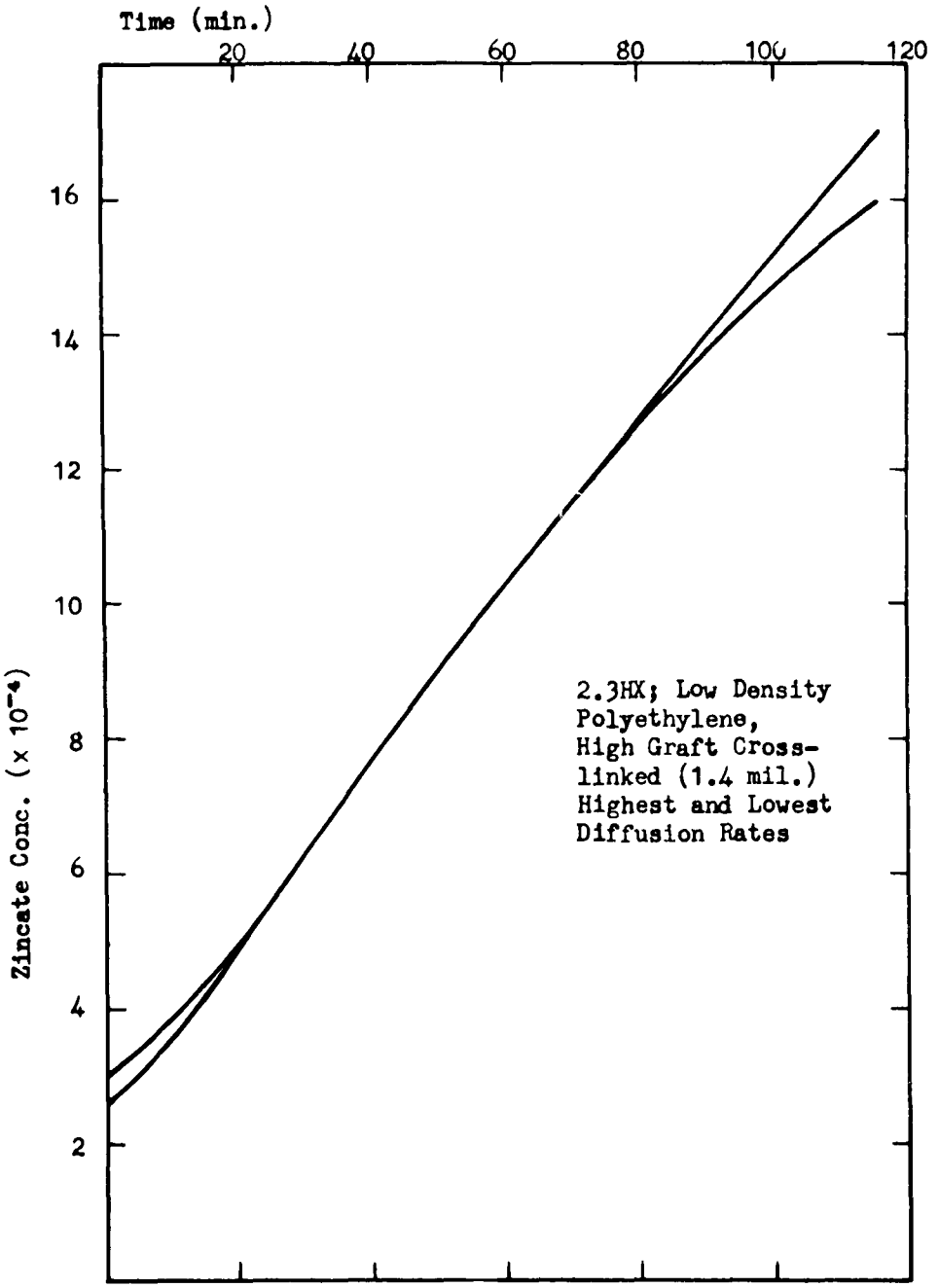

FIGURE 21 Zincate Concentration in 45% KOH by Diffusion Through Separator Materials

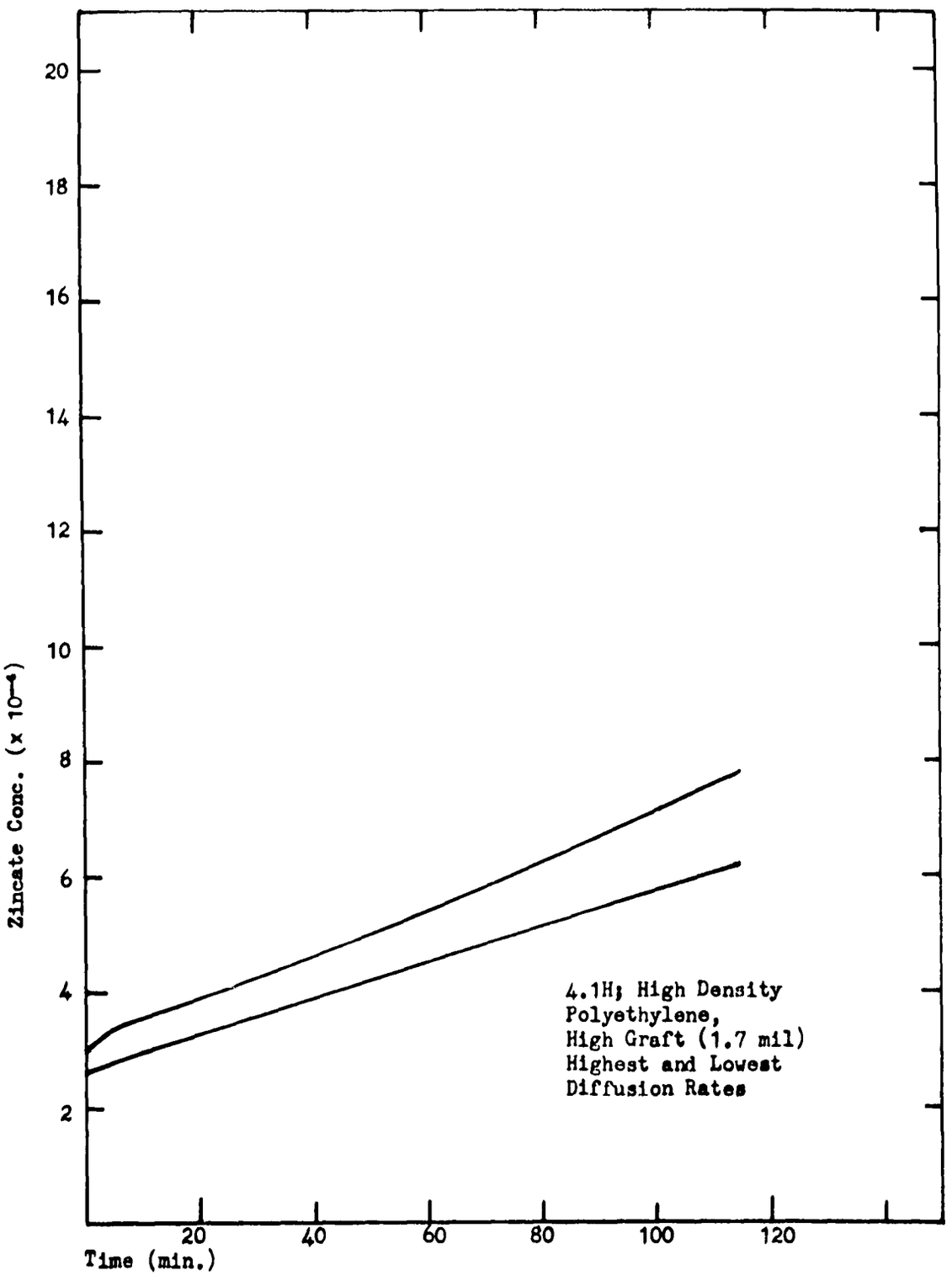

FIGURE 22 Zincate Concentration in 45% KOH by Diffusion Through Separator Materials

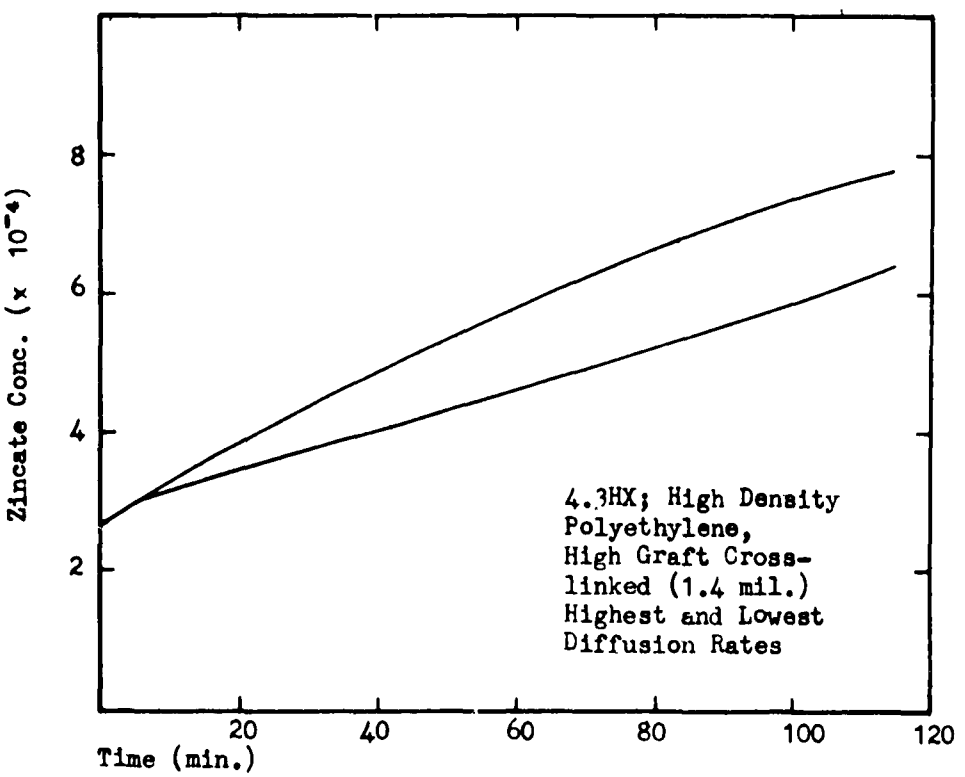

FIGURE 23 Zincate Concentration in 45% KOH by Diffusion Through Separator Materials

APPENDIX I

SILVER OXIDE-ZINC BATTERY SEPARATOR

VISKING COMPANY

NEW CELLULOSIC SEPARATORS FOR SEALED SECONDARY SILVER-ZINC ALKALINE BATTERIES

First Quarterly Technical Progress Report

Covering the Period

15 May 1963 - 1 August 1963

Dated

2 August 1963

Contract Nr. AF 33(657)-10643

Delco-Remy Purchase Order DR-317380

Research Department

Visking Company

Division of Union Carbide Corporation

Chicago, Illinois

Prepared by

Lloyd M. Cooke

FOREWORD

This report was prepared by the Visking Company Division of Union Carbide Corporation on Delco-Remy Purchase Order DR-317380 as a subcontract on Air Force Contract Nr. AF 33(657)-10643 under Task Nr. 817304-21.

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LIST OF ILLUSTRATIONS

ABSTRACT

Methods for determining pore sizes of Fibrous cellulosic membranes from water permeation measurements and from molecular diffusion data are described. Pore diameter data for regular (18-20 Å) and experimental (18-26 Å) Fibrous casings are presented.

An experimental Fibrous casing has been made with regenerated cellulose possessing a weight average molecular weight of about 150,000 (vs. about 100,000 for regenerated Fibrous casing) and a pore size comparable with regular Fibrous casings. A 100 foot sample of this casing has been shipped to Delco-Remy Division in fulfillment of Project Item B-1.

I. Introduction

The objective of this program is to determine theoretically and experimentally the fundamental properties required of fibrous cellulosic separator materials for silver-zinc batteries to enable improved design of long life, light weight sealed secondary batteries for military aerospace applications; and to synthesize and test new fibrous cellulosic separator materials possessing such fundamental properties.

The specific items to be studied under this contract are:

A. Preparation of Fibrous casing containing significantly higher and lower pore sizes than conventional Fibrous cellulosic separator materials to permit study of effect of pore size on silver penetration in cellulosic separators. Project Item A-1

B. Preparation of preoxidized and prereduced Fibrous casings to permit study of stabilization of functional groups on deposition of silver in cellulosic membranes. Project Item A-2

C. Preparation of carboxyl group-containing Fibrous casing membranes to permit study of the effect of permanent negative charge on the membrane on silver migration. Project Item A-3

D. Preparation of Fibrous casing containing ion exchange groups to permit study of the effect of such groups on silver migration. Project Item A-4

E. Preparation of Fibrous casings containing significantly higher molecular weight regenerated cellulose to permit determination of the effect of molecular weight on oxidative degradation of cellulosic separators. Project Item B-1

F. Preparation of preoxidized cellulosic membranes to evaluate its resistance to oxidative degradation. Project Item B-2

G. The preparation of fibrous cellulosic casing containing Ag+ ion and Ag metal to permit study of possible inhibiting action of silver on alkaline oxidative degradation of cellulosic membranes. Project Item B-3

This report covers initial work on Project Item A-1 and all work on Project Item B-1.

As the above samples are prepared and characterized by appropriate chemical and physical tests, they will be shipped to Delco-Remy Division of General Motors Corporation for further chemical and physical tests and for evaluation in silver-zinc batteries.

II. Factual Data

A. High and Low Pore Size Fibrous Cellulosic Casing (Project Item A-1)

1. Pore Size Measurements (Water Permeation):

The pore size of semi-permeable membranes is obtained from measurements of permeation rates of distilled water through membranes under a static pressure head of water. This method is based on Poiseuille's law for laminar flow through pipes with the assumption that the pores existing in the film are cylindrical in shape and are perpendicular to the film surface.[1) 2)] This assumption may be open to question; therefore, one is advised to treat such "pore size" data with caution, especially when comparing data from different membrane systems. Nevertheless, for the purposes of this investigation, which is concerned with a single species of membrane and where differences are primarily ones of porosity, relative pore size values are probably meaningful.

The equation used to determine pore size is:

$$r = 2L\sqrt{\frac{2\eta\frac{V}{A}}{PtW}}$$

where r = radius of the pore
L = film thickness
η = viscosity of water at 25°C.
V = the volume of water passing through an area A of the film in time t under a static pressure P
W = the volume of water absorbed per unit area of the film (pore volume per unit area)

The apparatus is shown in Figures 1, 2, and 3 and consists of a glass osmometer wherein a large surface area of film (11.7 cm^2) is exposed to water permeation. The film is partially supported on the low pressure side with wire gauze to prevent stretching of the film under a static pressure head of 25.75 cm. of water. The entire apparatus is suspended in a constant temperature bath (25°C.) of distilled water. Measurements consist of recording the time required for passage of a predetermined volume of water through the film. Consecutive permeation time measurements are taken until such become constant. In order to facilitate equilibration of the film with water, it is convenient to mount the membrane and permit it to soak in water overnight before commencing permeation time measurements.

The following data obtained with a sample of the control Fibrous casing membrane from the variable pore size study is typical of the experimental values and calculations employed:

Dry, Desulfured, Glycerine Free Fibrous Battery Separator Casings (Control Sample)

Temperature = 25 ± 0.1°C.
Viscosity of H_2O at 25°C. = 8.94×10^{-3} poises
Film wet thickness = 0.00541 in. (0.0137 cm.)
Water pressure (average) = 25.75 cm.
Volume of H_2O passed = 0.0036 ml.
Effective area of film exposed for permeation = 11.7 cm^2*

*Assumes that area in contact with supporting wire grid is impermeable.

Weight of film wet less weight dry = 0.0459 gm. of 1" diameter piece

Time intervals for test volumes of water to pass through membrane:

	29 minutes	4 seconds
	29 minutes	47 seconds
	29 minutes	24 seconds
	29 minutes	17 seconds
Average=	29 minutes	23 seconds = 1763 seconds

Using these values in the equation for pore radius

$$\text{pore radius} = 2 \times .0137 \sqrt{\frac{2\,(8.94 \times 10^{-3})\ \frac{.0036\ cm^3}{11.7\ cm^2}}{980.6\,(25.75cm.)\ \frac{0.0459\ gm.}{5.06cm. \times .997 \frac{gm.}{cc.}}\ 1763secs.}}$$

pore radius = 10.2 Å

pore diameter = 20.4 Å

2. Permeability Coefficient Measurements (Molecular Diffusion):

Theory -

By measuring the rates of diffusion of compounds possessing different molecular weights one can estimate the pore size of a membrane by relating this to the size of a molecule which just barely passes through the "pores" in the membrane. At the same time one can calculate permeability coefficients of different membranes to different ions to obtain data which may be useful in predicting performance of such membranes in electrodialysis and electrolytic cells.

This work has employed a cell similar to that described by Bieber, et al[3)4)] consisting of two chambers, one containing distilled water and the other a solution of a series of compounds of different molecular weights. The two chambers are separated by the membrane under test.

If one assumes that the concentration gradient across the membrane is linear, Fick's law of diffusion solved for non-stationary diffusion gives:

$$\log \frac{C_1^o}{C_1^o - 2C_2} = -\log\left(1 - \frac{2C_2}{C_1^o}\right) = \frac{2\ D_W\ A\ p}{2.303\ VL}\ t$$

Where p is the permeability coefficient of the diffusion species through the membrane under study; C_1 and C_2 are the molar concentrations in the concentrated and diluted solutions, respectively; C_1^o is the initial concentration of the concentrated solution, V is the volume of the concentrated solution; A is the exposed area of the membrane; L is the membrane thickness; t is the time; and D_W is the diffusion constant of the solute across a membrane-free solution-solvent interface.

The permeability coefficient represents that equivalent fraction of membrane area through which solute diffusion would be unrestricted. (One can also calculate a diffusion constant, D_M, of the solute across the membrane by multiplying its diffusion constant in water, D_W, by p, its permeability coefficient through the membrane.)

Determination of Solute Concentration -

The procedures for determining the concentrations of the different compounds used for diffusion measurements in water have been adapted from the following established analytical methods:

Urea is determined by converting to ammonia with urease and determining the ammonia by acid-base titration[5]; d-glucose and sucrose determined colorimetrically by Folin's ferricyanide method[6], protamine colorimetrically using Sakaguchi's tests for arginine[7] and hemoglobin spectrophotometrically.

Since some modification of each of the above analytical techniques has been necessary to adapt them to permeability coefficient measurements the detailed procedure for each of the compounds follows:

UREA

Reagents:

Urea stock solution - 1.0%, reagent grade

Urease solution - 0.1% (stored in refrigerator)

HCl, 0.1 N, standardized

NaOH, 0.1 N, standardized

Procedure:

(1) Two ml. of solution removed from the low concentration side of the cell with a pipette are diluted to approximately 75 ml. with boiled distilled water in a 250 ml. beaker.

(2) Ten ml. of 0.1% Urease solution are added to the contents of the beaker and the solution allowed to stand one hour at room temperature.

(3) Exactly 5.0 ml. standard N/10 HCl are added to the solution which is then sparged with nitrogen gas for about ten minutes to remove carbon dioxide formed during the conversion of urea to ammonia.

(4) The excess HCl is then back-titrated with standard N/10 NaOH to that pH value previously determined on a blank consisting of 10 ml. of urease solution subjected to procedure steps (2) and (3) omitting the HCl addition.

(5) The amount of urea present is then determined from the amount of hydrochloric acid neutralized as follows:

$$\frac{\text{Gms. Urea}}{\text{ml.}} = 1.5 \times 10^{-3} (\text{ml. of HCl neutralized})$$

D-GLUCOSE (DEXTROSE)

Reagents:

Glucose stock solution - 0.1%, reagent grade

Potassium ferricyanide solution - 0.2%

Sodium cyanide - carbonate solution - A solution of 8 g. of anhydrous sodium carbonate in 50 cc. of water is mixed with 150 cc. of a freshly-prepared 1% solution of sodium cyanide and the mixture diluted to 500 cc. with distilled water.

Ferric iron solution - A copper wire screen supporting 20 grams of soluble gum ghatti is suspended in 1 liter of distilled water overnight. The screen is then removed and the solution filtered through cheese cloth. Five grams of anhydrous ferric sulfate are dissolved in a mixture of 75 cc. of 85 percent phosphoric acid and 100 cc. of distilled water and added to the gum ghatti solution. Sufficient 1 percent potassium permanganate solution is then added to remove any reducing material present so that a slight pink color will persist for about five minutes. Care should be taken so that no pink color remains when the solution is used.

Procedure:

(1) Two ml. of solution removed from the low concentration side of the cell with a pipette are diluted to 25 ml. in a volumetric flask.

(2) Five ml. of this diluted solution are placed in a 25 ml. volumetric flask and 1 ml. of the ferricyanide solution and 1 ml. of the cyanide-carbonate solution are added.

(3) The volumetric flask is then heated exactly eight minutes in a boiling water bath and then cooled for two minutes in tap water.

(4) Five ml. of the ferric iron solution are added, the solution mixed, and allowed to stand for five minutes before diluting to 25 ml. with distilled water.

(5) The absorbance of this solution is then determined at 698 mμ.

(6) All of the above steps are repeated for a blank containing distilled water instead of the glucose solution.

(7) The absorbance of the glucose test sample is corrected by subtracting the absorbance of the blank. The corrected absorbance value is used directly for permeability coefficient calculations since absorbance is directly proportional to concentration at the concentrations employed in these tests.

(8) For convenience, the absorbance of the glucose solution (0.1%) is best determined after diluting twenty-fold.

SUCROSE

Reagents:

Sucrose stock solution - 0.5% reagent grade

HCl - 0.1 N solution

NaOH - 0.2 N solution

Potassium ferricyanide solution - (see glucose determination)

Sodium cyanide - carbonate solution (see glucose determination)

Ferric iron solution - (see glucose determination)

Procedure:

(1) Two ml. of the solution pipetted from the low concentration side of the cell are placed in a 25 ml. volumetric flask and 8 ml. distilled water are added.

(2) Two ml. of N/10 hydrochloric acid are added and the solution heated in boiling water for thirty minutes to hydrolyze the sucrose.

(3) The solution is cooled and 1 ml. of 0.2 N sodium hydroxide solution added. The solution is then diluted to 25 ml. using distilled water.

(4) Three ml. of this solution are placed in a 25 ml. volumetric flask and 1 ml. of the ferricyanide solution and 1 ml. of the cyamide-carbonate solution added. The colorimetric procedure described above for d-glucose is then followed.

(5) The absorbance of the 0.5% stock sucrose solution (0.5%) is conveniently determined using a twenty-fold dilution prior to hydrolysis.

PROTAMINE SULFATE

Reagents:

Protamine sulfate stock solution - 0.2 percent

KOH solution - 10%

Urea solution - 40%

α-naphthol in 50% ethyl alcohol - 0.1%

Potassium hypobromite - 2 grams bromine in 100 ml. of 5% KOH

Procedure:

(1) Two ml. of the solution from the low concentration side of the cell are placed in a 25 ml. volumetric flask and diluted with 8 ml. distilled water.

(2) One ml. of 10% KOH, 2 ml. of the α-naphthol solution, and 1 ml. of the urea solution are added and the solution cooled with tap water if necessary.

(3) One ml. of the hypobromite solution is added with swirling to prevent local excess.

(4) Three minutes after this initial addition, 1 ml. of urea solution and 1 ml. of hypobromite solution are again added to produce maximum color formation.

(5) The solution is then diluted to 25 ml. with distilled water and allowed to stand eighteen minutes from the initial addition of hypobromite.

(6) The absorbance of the solution is then determined at 521 mμ.

(7) A blank is run using distilled water in place of the protamine solution.

(8) As in the sugar determinations, absorbance values can be used directly in the equation used to calculate permeability coefficients.

(9) One ml. of the stock solution is sufficient for determining its absorbance value.

Molecular Diffusion Cell and Procedure for Determining Diffusion Rates

The diffusion cell used in these experiments is shown in Figures 4, 5 and 6. It consists of two chambers one of which is filled with distilled water and the other with an aqueous solution of the compound under test. The membrane diffusion area is controlled by the dimensions of the

orifice plate. A 2-1/2 inch diameter orifice yielding a 32.7 sq. cm. membrane area is used in this work. The contents of each chamber is stirred through the hole in the top of the chamber. Samples are also withdrawn through the same holes.

The general procedure used for determining the rate of molecular diffusion through membranes is as follows:

(1) The cell is assembled as rapidly as possible (3-4 minutes) with the shiny side of the Fibrous casing membrane facing the high concentration side of the cell, and the cell is placed in a constant temperature ($25^{o}C.$) bath.

(2) Glass propellor stirrers connected to variable speed electric motors are inserted into each of the two chambers to a depth about midway down the cell.

(3) Two hundred ml. of the stock solution of the compound under study and 200 ml. of distilled water are added to each of the two chambers, respectively, at the same time to avoid stretching the membrane. If the chambers are not completely full, add and record the necessary additional liquid.

(4) The stirrers are then started and operated at 500 RPM, or faster, to avoid concentration gradients elsewhere than in the membrane itself.

(5) At least four 2.00 ml. samples are withdrawn from the dilute solution cell at various appropriate time intervals for analysis. The following sampling time intervals have been found convenient with Fibrous casing membranes:

Diffusing Molecule	Molecular Weight	Molecular Diameter (Å)	Initial Sample (Hrs. after start)	Additional Sampling Intervals (Hrs.)
Urea	60	5.4	1	0.75
d-Glucose	180	7.2	2	1.5
Sucrose	342	8.8	2	2
Protamine Sulfate	2000-8000	24.0	5	8
Hemoglobin	67,000	60.0	72	8

3. Pore Size Permeability Data on Experimental Fibrous Casings

In the program to prepare new experimental fibrous cellulosic casings possessing higher and lower pore size than regular fibrous casings for batteries, Visking proprietory process conditions were altered first very slightly, and then more pronouncedly as pore size data was accumulated. All experimental casings for this work were extruded, processed and dried on plant equipment. All casings were desulfured, and dried without glycerine.

Those experimental fibrous casings obtained from runs extruded to yield lower than normal sized pores are coded LPS, and those extruded to yield higher than normal pore size, HPS.

Water permeation pore size data for key experimental runs are included in Table 1. Differences in pore sizes between experimental casings and control casings were always in the expected direction. Only limited permeability coefficient data have been collected thus far. Complete data will be included in the next Quarterly Report.

The pore size of sample HPS-3 (26.6 Å as contrasted with 18.0-20.0 Å for control casings) appears suitable for the purpose of this project; therefore, a 100 foot dried glycerine-free desulfured sample of small casing is being prepared.

The pore sizes on the smaller than regular casings prepared thus far are not as small as desired; therefore, work to obtain this material is continuing.

B. Fibrous Casing with High Molecular Cellulose-Project Item B-1

One hundred feet of dried glycerine-free desulfured Fibrous casing made with cellulose possessing a C.E.D. viscosity* of 7.28 centipoises ($M.W._w$, or weight average molecular weight, about 150,000) has been prepared by our regular process and shipped to Delco-Remy. A 100 foot sample of control shipped at the same time was prepared with normal molecular weight (ca. 100,000) viscose.

*0.5% cupriethylenediamine viscosity - Tappi #230.

The water permeability pore diameter values for the two casings were found to be 18.2 Å and 20.4 Å, respectively.

III. Conclusions

Equipment and experimental conditions are described for determining pore sizes from water permeation measurements and permeability coefficients from molecular diffusion data for Fibrous regenerated cellulose membranes.

Initial work on the preparation of experimental Fibrous casing possessing higher and lower pore size than normal for Project Item A-1 has lead to a process for casings with pore diameters about 26 Å for regular Fibrous battery separator casings. Preparation of a 100 foot sample of such casing is underway. Development work on lower pore size material is continuing.

A 100 foot sample of Fibrous casing based upon cellulose possessing higher than normal molecular weight ($M.W._w$ = 150,000 vs. 100,000 for normal cellulose) has been prepared and shipped to Delco-Remy to complete the Visking phase of Project Item B-1.

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3) H. H. Bieber, P. F. Bruins, and H. P. Gregor, Industrial and Engineering Chemistry, 50, 1273 (1958).

4) R. M. Barrer, Diffusion In and Through Solids, Cambridge, England; The University Press, 1941.

5) J. M. Mitchell, Jr., et al, Organic Analysis, New York: Interscience Publishers, Inc., 1960, Vol. IV, pg. 81.

6) W. D. Stovall, M. Foote, and M. S. Nichols, American Journal Clinical Pathology, 3, 299 (1933).

7) H. T. Macpherson, Biochemical Journal, 36, 59, (1942).

Table 1

Pore Diameters of Experimental Fibrous Cellulosic Casings

Sample Number	Visking Run Number	Rewet Gel Swell (%)	Rewet Thickness (Mils)	Time for Water Passage (Minutes)	Calculated Pore Diameter (Å)
LPS-1	2A-63	99	5.54	36.1	19.2
LPS-1-Control	2C-13-64	101	5.44	28.9	20.8
HPS-1	3A-10	99	5.76	37.2	19.7
HPS-1-Control	3A-11	103	4.98	32.2	18.0
HPS-2	4A-14	106	5.67	36.0	19.2
LPS-2	5A-19	107	5.74	39.4	18.1
HPS-3	6A-52	118	4.55	16.2	26.4

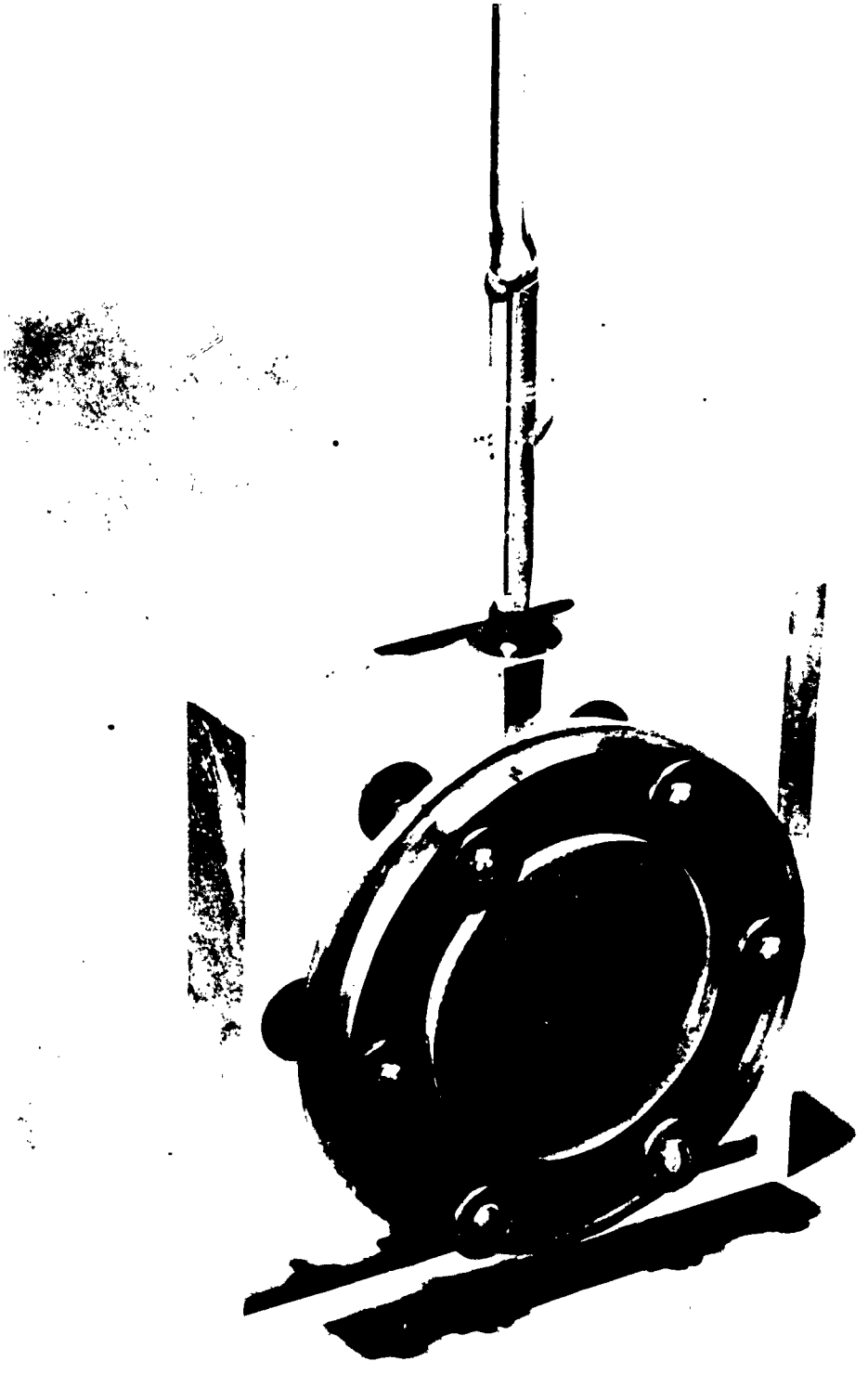

FIGURE 1 Water Permeation Cell

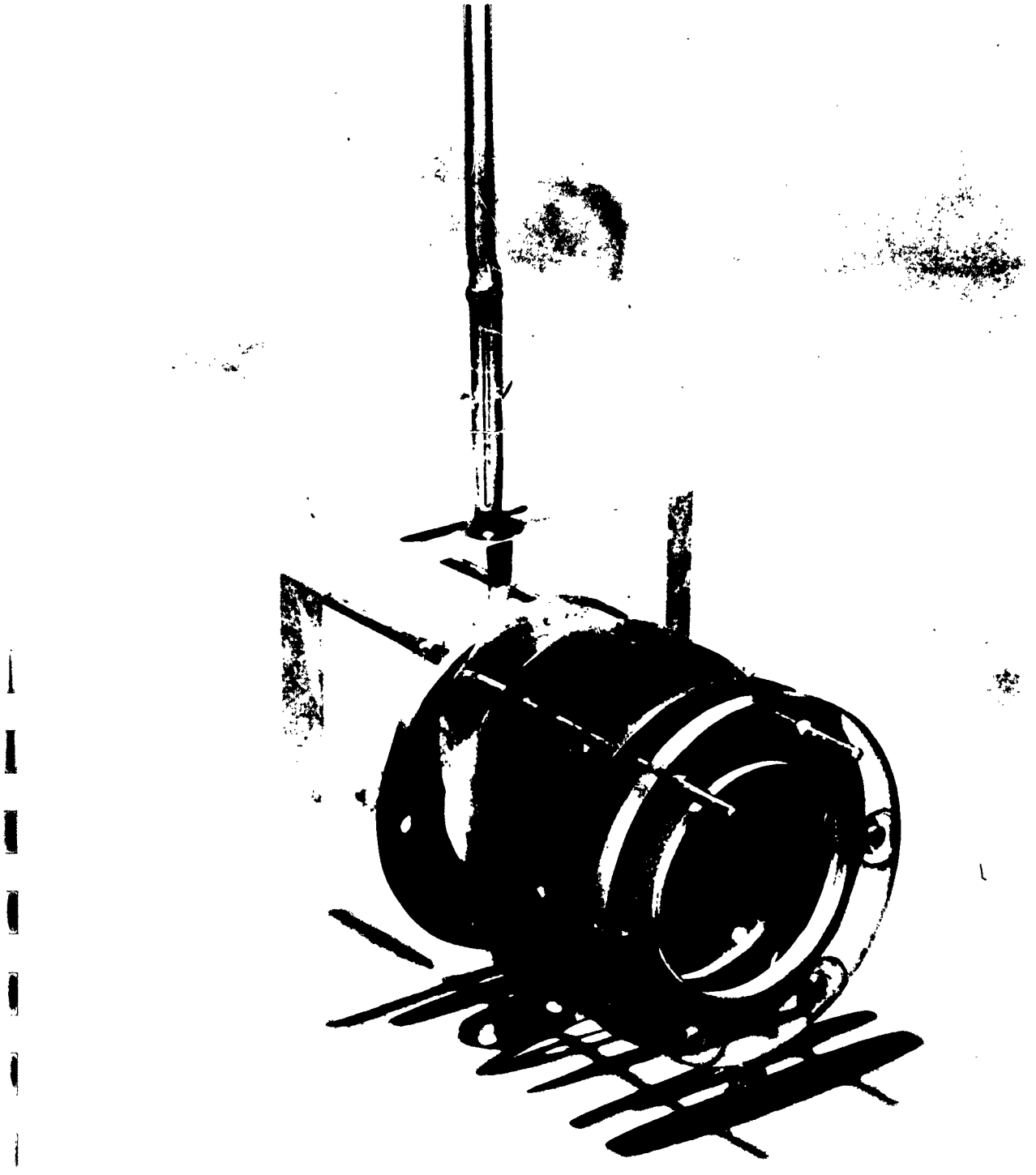

FIGURE 2 Water Permeation Cell - Exploded View

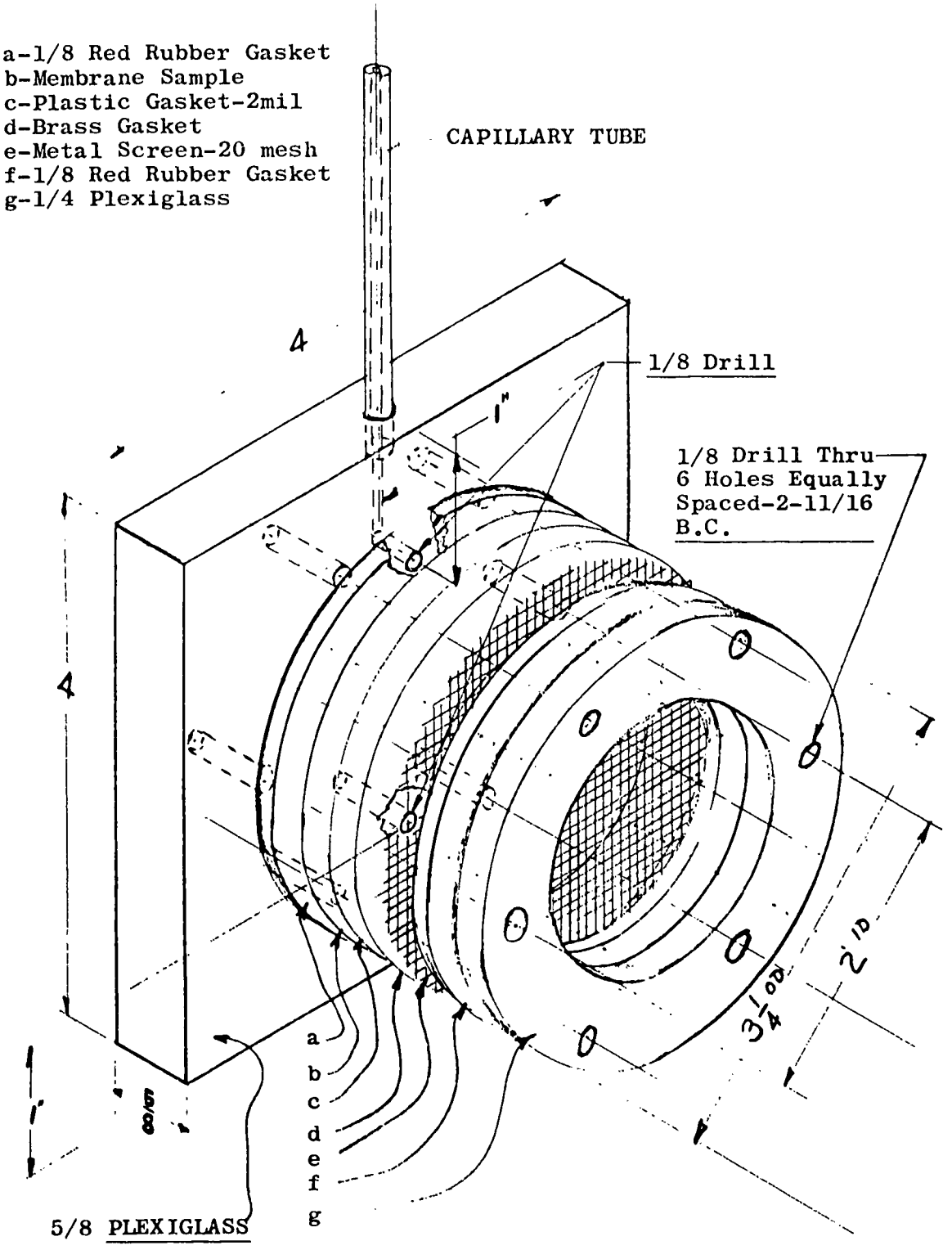

FIGURE 3 Water Permeation Cell

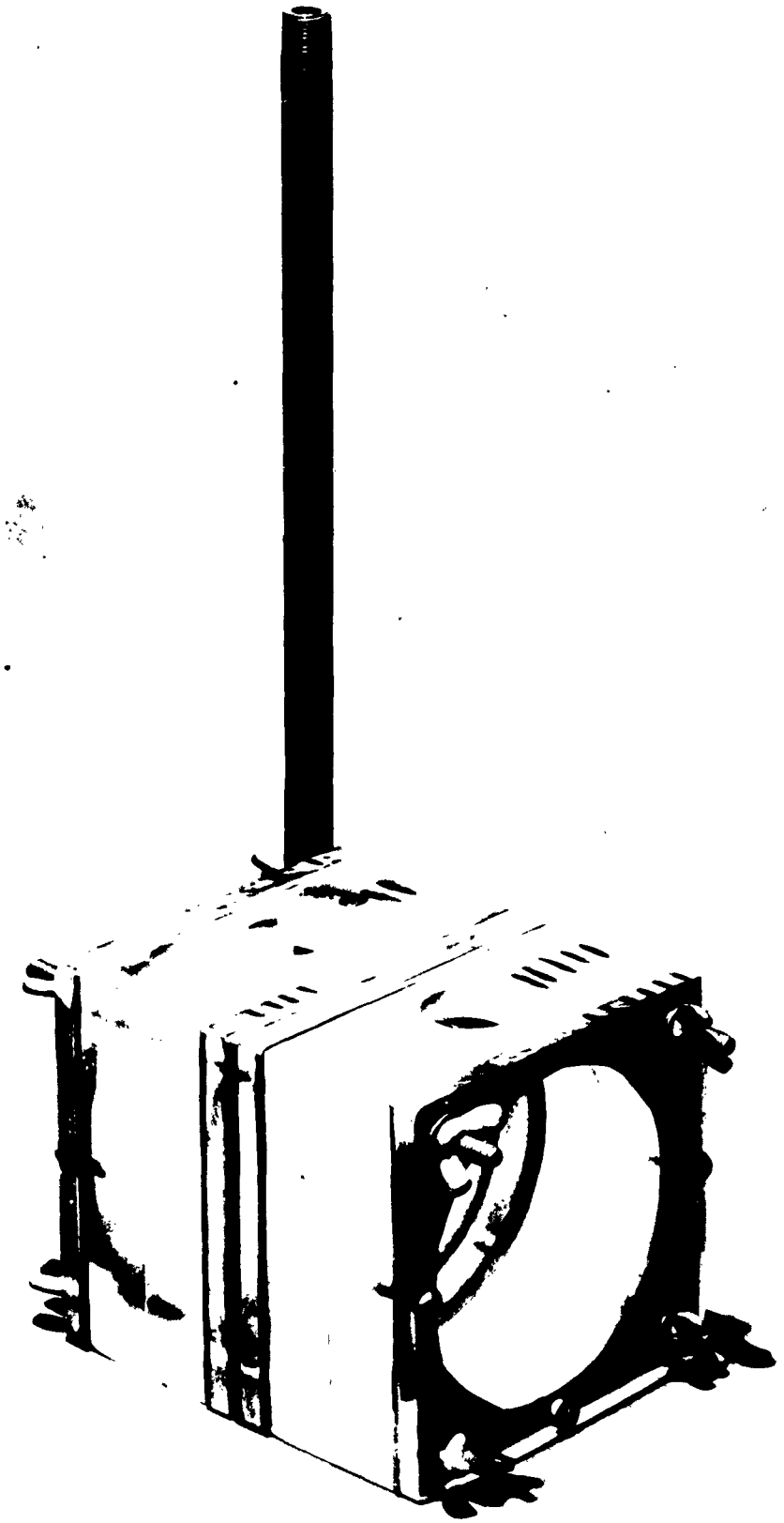

FIGURE 4 Molecular Diffusion Cell

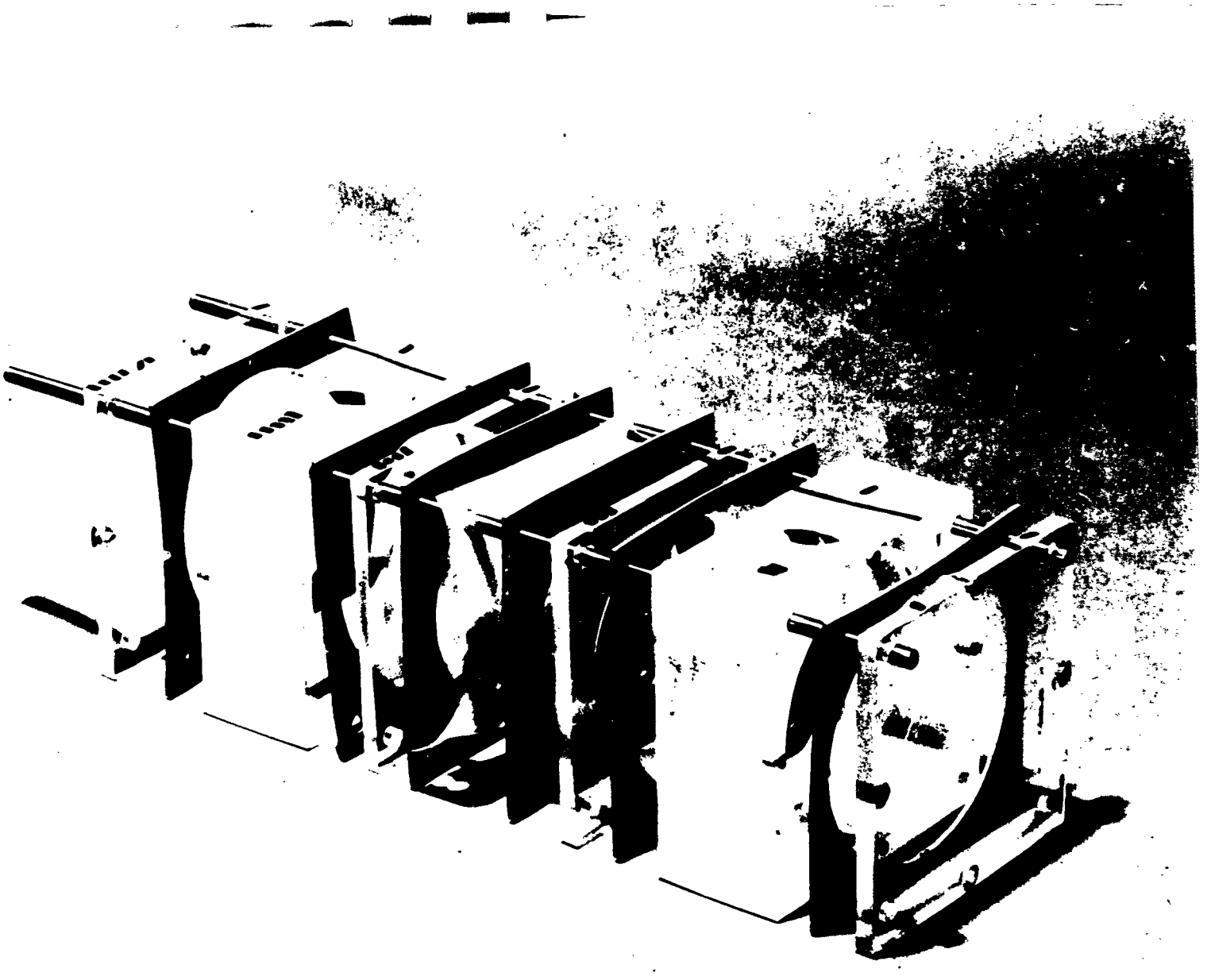

FIGURE 5 Molecular Diffusion Cell - Exploded View

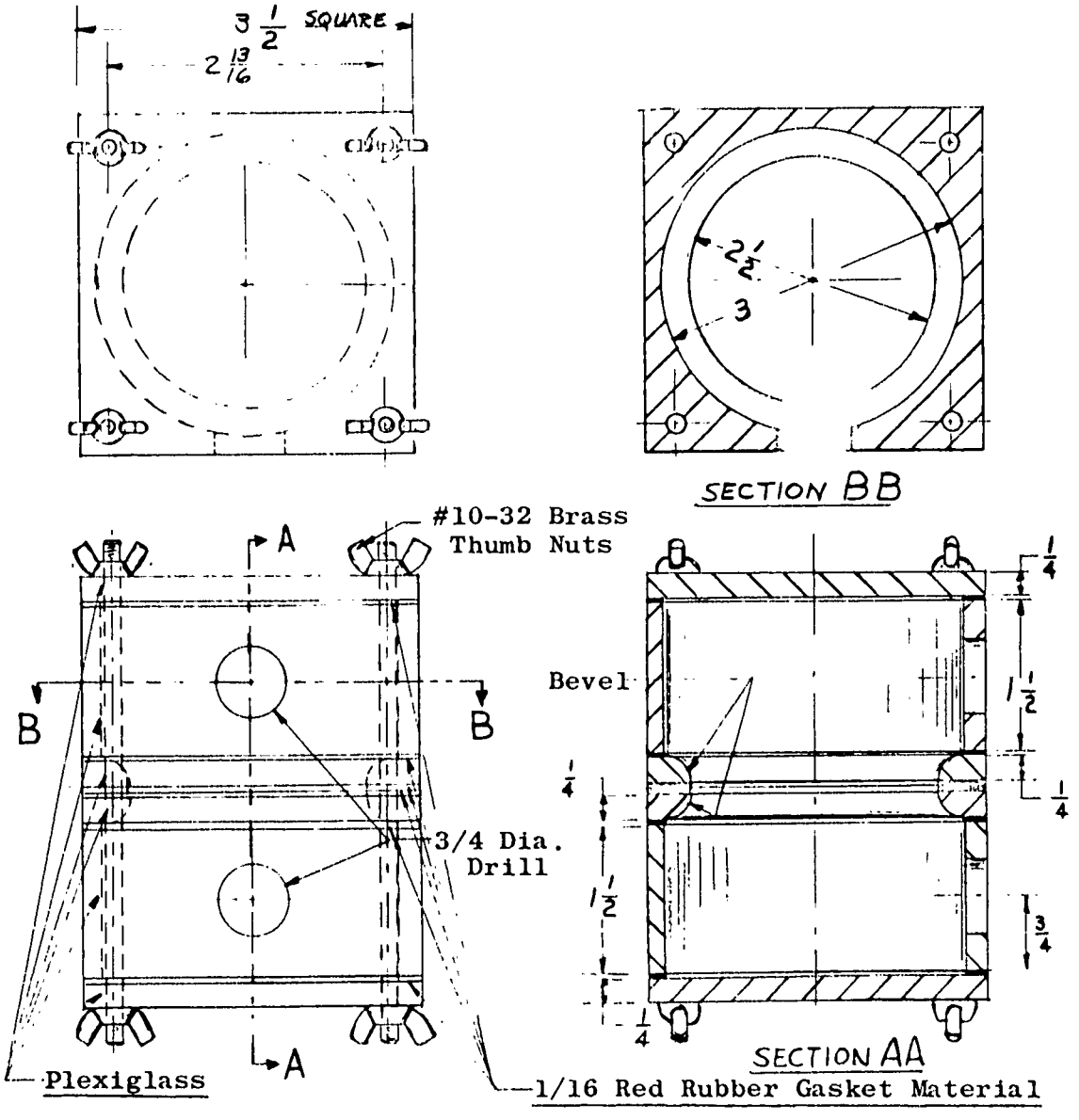

FIGURE 6 Molecular Diffusion Cell

APPENDIX II

SILVER OXIDE-ZINC BATTERY SEPARATOR

RADIATION APPLICATIONS INC.

"Silver Oxide - Zinc Battery Separator"

First Quarterly Technical Progress Report

Covering the Period

1 May 1963 to 1 August 1963

Dated

26 July 1963

AF Contract Nr. AF 33(657)-10643

on Delco-Remy Purchase Order

Mr. DR-314307

Radiation Applications Incorporated

Long Island City, N. Y.

Prepared by

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LIST OF ILLUSTRATIONS

ABSTRACT

Six samples have been submitted to Delco-Remy for evaluation. Samples based on polyvinylidene fluoride (PVF_2) are not usable as these membranes are rapidly attacked by potassium hydroxide. Fluorinated ethylene-propylene copolymer (FEP Teflon) samples are to be substituted for the PVF_2 samples.

The test procedures have been established except for the dialysis phase of the pore size determination, which was delayed. Sample characterizations have been started.

I. Introduction

This report covers the first three months of the ten month program.

The work in this period was devoted to the development of preparative procedures for, and the preparation of, experimental membranes with controlled basic membrane parameters, and towards the development of methods for the determination of these membrane parameters.

The sample preparation phase is progressing on schedule, and six samples, described in the body of this report, have been delivered to Delco-Remy. Membranes based on polyvinylidene fluoride are an exception. These have proven subject to attack by 40% KOH. FEP Teflon will be substituted for this material to provide the required number of samples.

The characterization phase is lagging behind schedule, but all tests are expected to be operative by the end of the next month.

II. Factual Data

1.0 Membrane Preparations

No insoluble difficulties have been encountered to date, save in the case of the polyvinylidene fluoride membranes.

Two problems have been encountered with this material. First of all it has proven to be exceedingly difficult to obtain sufficient graft to produce membranes with electrical resistances compatible with the requirements of battery operation. Second, and more significantly it has been observed that the grafted PVF_2 films turn from a translucent white to jet black in a matter of seconds upon immersion in 40% KOH. This color development is thought to be a result of the stripping off of HF from the polymer by the KOH. It is apparently progressive as the films rapidly lose strength.

The preparative procedures for each of the samples submitted to Delco-Remy to this writing are presented below.

High Graft Level, Low Density Polyethylene (Sample 2.1H)

Preparative Procedure

Materials: A. 1 mil low density (0.922) polyethylene film

B. Glacial Acrylic Acid (0.02% MEHQ)

C. Toluene, xylene or benzene

D. Carbon tetrachloride

E. Paper toweling

Procedure:

1. The polyethylene film and paper toweling are rolled up into a double helix so that the paper toweling serves to separate the layers of polyethylene.

2. Prepare a mixture of B, C, and D so that the proportions are: B = 25%, C = 70%, and D = 5% by volume.

3. Place the film roll into a suitable container and fill with the solution prepared in step 2.

4. Place the sample into a Co^{60} source so that it is irradiated at a dose rate of 16,000 rads/hr, and exposed to a total dose of 1.6 Mrads.

5. After removing the sample roll from the source, the grafted film is separated from the paper toweling and washed free of clinging homopolymer by soaking for three hours in a 5% KOH solution. The washed film is then rinsed with water and dried.

Low Graft Level, Low Density Polyethylene (Sample 2.1L)

Preparative Procedure

Materials: A. 1 mil low density (0.922) polyethylene film

B. Glacial acrylic acid (0.02% MEHQ)

C. Toluene, benzene or xylene

D. Carbon tetrachloride

E. Paper toweling

Procedure: 1. to 3. Same as in preparation 2.1H.

4. Place the sample into a Co^{60} source so that it is irradiated at a dose rate of 16,000 rads/hr and exposed to a total dose of 0.8 Mrads.

5. Proceed as in preparation 2.1H.

Low Density Polyethylene - High Graft Post Graft Crosslinked (Sample 2.3HX)

Preparation Procedure

Materials: A. A portion of sample 2.1H.

Procedure: 1. The grafted film is passed under the beam of 2 Mev. electron accelerator (Van der Graaff).

2. A dose rate of 2 Mr/pass is used.

3. Time is allowed (10 min.) after each pass so that the film can re-equilibrate with the atmospheric moisture.

4. A total dose of 30 megarads is used.

High Density Polyethylene - High Graft (Sample 4.1H)

Preparative Procedure

Materials: A. 0.9 mil high density (0.96) polyethylene Film

B. Glacial acrylic acid, 0.02% MEHQ

C. Toluene, xylene or benzene

D. Cheesecloth

Procedure: 1. Roll A and D together in a tight double helix.

2. Prepare a mixture of B and C such taht B = 25% and C = 75% by volume.

3. Place the film roll (1) in a suitable container and fill with the B-C solution from step 2.

4. Place the container in proximity to a Co^{60} source so that the gamma dose rate it receives is 50,000 rads/hr. Continue the exposure until a dose of 1.25 megarads is accumulated.

5. Remove the film from the container and wash free of clinging homopolymer with a 5% KOH solution.

6. Rinse with water and dry the film at 40°C for 4 hours.

High Density Polyethylene - High Graft Post Graft Crosslinked (Sample 4.3HX)

Preparative Procedure

Materials: A. A portion of sample 4.1H

Procedure: 1. The grafted film is passed under the beam of a 2 Mev. Van der Graaff electron accelerator.

2. A dose rate of 2 Mr/pass is used.

3. Time is allowed (10 min.) after each pass so that the film can re-equilibrate with the atmospheric moisture.

4. A total dose of 30 megarads is used.

Teflon TFE - High Graft (Sample 5.1H)

Preparative Procedure

Materials: A. 1 mil fusion cast TFE Teflon film

B. Glacial acrylic acid, 0.02% MEHQ

C. Toluene, xylene or benzene

D. Paper Toweling

Procedure: 1. Roll A and D together in a tight double helix.

2. Prepare a mixture of B and C such that B = 25% by volume and C = 75% by volume.

3. Place the film roll (1) in a suitable container and fill with the solution from step (2).

4. Place the container in proximity to a Co^{60} source so that the gamma dose rate it receives is 25,000 rads/hr. Continue the exposure until a dose of 0.75 megarads is accumulated.

5. Remove the film from the container and wash free of clinging homopolymer with a 5% KOH solution.

6. Rinse with water and dry the film at 40°C for 4 hours.

7. Repeat steps (1) - (6) but using the grafted film obtained above instead of untreated Teflon.

2.0 Characterization Phase

The purpose of this phase is to measure some of the fundamental parameters of the separator membranes prepared under this contract.

The parameters to be determined as functions of the preparative variables are:

A. Percent Graft

B. Dimensional Changes Upon Wetting

C. Durability in 40% KOH

D. Oxidation Resistance

E. Tendency to "Load" with Metallic Silver

F. Silver Permeability (to Dissolved Silver Oxides)

G. Porosity

H. Average Pore Size

I. Electrical Resistance in 40% KOH.

2.1 Analytical Procedures

A. Percent Graft

Percent graft is determined indirectly. The exchange capacity of a 6" x 6" sample is determined, and the percent graft is back-calculated from the result.

(a) A six inch by six inch sample is cut and equilibrated 24 hours in a large excess of ca. 0.1N HCL to place the membrane in its acid form.

(b) The sample is dried 2 hours at 60°C and weighed.

(c) The sample next is placed in 100 ml. of standardized KOH solution, and again equilibrated for 24 hours.

(d) An aliquot of the KOH solution in which the sample has been equilibrated is then titrated with standardized HCl to determine the change in concentration due to neutralization of the membrane sample.

(e) The exchange capacity of the sample is then simply calculated from the equation

$$\text{Exchange capacity} = \frac{(\text{N orig. KOH} - \text{N final KOH}) \times 100}{\text{dry wt. of sample (acid form)}}$$

$$= \text{meg/gm}$$

(f) Percent graft is then expressed as

$$\% \, G = \frac{\text{FW acrylic acid} \times \text{exchange cap.}}{1 - [\text{F W acrylic acid} \times \text{ex. cap.}]}$$

$$= \frac{72.06 \times \text{ex. cap.}}{1 - [72.06 \times \text{ex. cap.}]}$$

B. Dimensional Changes Upon Wetting with 40% KOH

A steel rule with 1/64" divisions and a caliper micrometer estimable to $\pm$ 0.00025 inch are used for this test.

(a) A two inch by three inch sample in its potassium salt form is cut.

(b) The sample is dried for two hours at 45°C and its dimensions determined.

(c) The sample is then equilibrated in 40% KOH for two hours and its dimensions again determined. The percent changes in length, width, and thickness are reported.

C. Durability in 40% KOH

The object of this test is to obtain a comparative series of tensile strength data as a function of time in hot 40% KOH for all the membranes prepared.

The test will be set up such that the samples are aged in 160°F 40% KOH. Duplicate samples of each membrane will be run at each interval of time. These intervals will be: 3 hrs, 6 hrs, 24 hrs, 48 hrs, 1 week, 2 weeks, 3 weeks, 4 weeks.

A Dillon Tester will be used for the tensile strength determinations. This test will not commence until all samples have been prepared.

D. Oxidation Resistance

E. Tendency to "Load" with Metallic Silver

F. Permeability to Dissolved Silver Oxides

These tests are all run in the cell shown in Figure 1. The cell consists of two silver-oxide electrodes, one inch by one inch, held in lucite clamps. The electrodes are so charged that initially one has a capacity of 300 m.a.h. and the other 100 m.a.h.

For tests D and E the sample membrane is inserted in the cell as shown in Figure 1A, directly in contact with the two electrodes.

The cell, immersed in 40% KOH, is placed in an oven set at 110°F, and two hundred milliamperes are passed in alternate directions, for one hour in each direction.

The p.d. across the cell is continuously monitored by means of recorders. The test is stopped after one hundred hours or when a short is observed. The circuitry is shown in Figure 3.

For test D the sample is removed and examined visually and mechanically for signs of deterioration.

For Test E the sample is examined visually for silver, and the electronic resistance through the dried sample is measured in the most heavily silvered areas. The sample finally is ashed and any silver present picked up in nitric acid. The quantity of silver present is then determined using the procedure described below under test F.

For test F the cell is assembled as in Figure 1B, using a layer of cellophane as an indicator layer. The cell is cycled in the same manner as in tests D and E. At the end of one hundred hours the silver content of the cellophane is determined using the following procedure:

(a) Preparation of calibration curve for the modified Volhard silver analysis.

(1) Prepare one liter of ca. 0.1 N KCNS (one liter is enough for 4000 determinations).

(2) Dilute 10 ml. of the stock 0.1 N KCNS solution to 1 liter in a volumetric flask to prepare ca. 0.001 N KCNS.

(3) Prepare a series of silver solutions in 100 ml. volumetric flasks, each containing 3 ml. 0.1 N $Fe(NO_3)_3$, so that the solutions cover the range of 0.5 to 10 mgm Ag/100 ml.

(4) Transfer a 25 ml. aliquot of each silver solution to individual erlenmeyer flasks and to each one add 25 ml. 0.001 N KCNS slowly dropwise while rapidly stirring.

(5) Filter and read the transmittance of each solution at 550 mu on a Bausch and Lomb Spectronic 20 Colorimeter.

(6) Plot log (T %) vs. mgm Ag/100 ml (see Figure 4).

(b) Ash the entire membrane sample in a covered Coors porcelain crucible.

(c) Digest the ash in 10 ml. of ca. 1 N HNO_3.

(d) Filter and transfer quantitatively to a 100 ml. volumetric flask. Add 3 ml. of 0.1 N $Fe(NO_3)_3$ acidulated with HNO_3 and bring the volume to 100 ml. with de-ionized water.

(e) To a 25 ml. aliquot of the silver-$Fe(NO_3)_3$ solution add slowly dropwise 25 ml. 0.001 N KCNS with rapid stirring.

(f) Filter through No. 00 filter paper and read the transmittance of the solution at 550 mu using the Bausch and Lomb Spectronic 20 Colorimeter.

(g) The silver content in milligrams of the titrated aliquot is read from the previously prepared calibration curve.

If the sample should fall beyond the upper limits of the curve, take a suitably smaller aliquot of the remaining silver solution, dilute it to 25 ml., and re-run the analysis. If the sample should fall below the lower limit of the curve, add a known amount of silver to the remaining solution to bring the silver content into the readable range and repeat the analysis.

G. Porosity

The porosity of the film must be known both as water swollen, for the pore size determination, and also as swollen with 40% KOH.

To determine porosity, the wet volume of the film and the volume of the pore solution must botn be determined.

The volume of the pore solution is readily obtained by weighing the film dry, wet, and after re-drying. One assumes here, of course, that all of the imbibed solution is present as free pore solution and that there are no density gradients existing in the solutions within the "pores".

The wet volume of the film is not so readily obtainable with any accuracy. Physical measurements of the film dimensions lack sufficient resolution to show small volume differences as do methods based upon weighing a displaced liquid.

The presently most encouraging approach is to perform a density titration. With this method, a weighed sample of wet film (with blotted surfaces) is placed into a cylinder with a liquid whose density is such that the sample sinks to the bottom. A miscible

liquid of very high density is then titrated in until the density of the film is matched by the surrounding medium. This point is easily observed as that point at which the film neither floats nor sinks but remains suspended at any level at which it is placed. The density of the medium is then determined by standard means.

H. Pore Size

To estimate the average pore size, dialyses of two solutes of differing molecular weights (molecular diameters) are run.

From the mass transfer data for each solute, dialysis coefficients are determined. Using suitable equations, relating the dialysis coefficients to the film thickness, porosity, pore-tortuosity and the ratio of the molecular diameters of the dialyzing species to the pore diameters, one estimates the average pore size of the sample film.

This test has been delayed due to slow delivery of acceptable dialysis cells. These are now in-house (see Figure 5).

The analytical techniques for the two solutes to be used in this study are described below.

(a) Sucrose Analyses

The analysis is based upon the reduction of Fehlings solution by the action of acid hydrolyzed sucrose. The procedure is as follows:

(1) Prepare Fehlings solution A by dissolving 69.28 gms. of $CuSO_4$ in 800 ml. of de-ionized water in a 1 liter flask. Adjust the volume to 1 liter.

(2) Prepare Fehlings solution B by dissolving 120 gms. NaOH and 346 gms. sodium-potassium tartarate in 800 ml. of de-ionized water in a 1 liter volumetric flask and adjust the level to 1 liter.

(3) Weigh out pure sucrose, previously dried overnight in a vacuum dessicator, to make up an accurately known solution in the vicinity of 1.0% concentration.

(4) To a 75 ml. aliquot of the sucrose solution add 10 ml. 0.5 N HCl and heat at 68° - 70°C. for 20 minutes.

(5) Cool and neutralize with 0.5 N NaOH solution.

(6) Transfer quantitatively to a 250 ml. volumetric flask and bring to 250 ml. with boiled-out de-ionized water.

(7) Dilute 10 ml. of the Fehlings solution to about 20 ml. with water and titrate with the hydrolyzed sucrose solution to obtain a rough end point (disappearance of blue color). The Fehlings solution consists of a mixture of equal volumes of Fehlings solution A and Fehlings solution B.

(8) Titrate with the sucrose solution to within 2 ml. of the rough endpoint and boil for another minute. Then add the sucrose solution in 2 drop intervals boiling for 30 seconds between additions until the endpoint is reached.

(9) Step 8 may be repeated twice to obtain a more precise endpoint.

(10) Repeat steps 4 through 9 with two different concentrations of sucrose to verify the equivalency of the Fehlings

solution.

$$\text{Titer} = \text{gms sucrose/ml Fehl. solu.} = \frac{\frac{\text{gms Sucrose}}{250 \text{ ml.}} \times \text{vol titrant}}{20 \text{ ml}}$$

(11) Having standardized the Fehlings solution, the unknown samples are analyzed by repeating steps 4 through 9.

(b) Urea Analyses

In this determination, the urea is converted to free ammonia by the enzyme urease. The ammonia is then reacted with hypochlorite ion to form chloramine. The chloramine then is reacted with phenol to yield the indophenoxide anion (blue). The optical density of the solution is then read at 625 mu on the Bausch and Lomb Spectronic 20 Colorimeter.

The method is extremely sensitive and is employed on samples containing 1 - 5 micrograms of ammonia equivalent. The low concentrations are achieved by suitable dilutions of the samples.

The analyses are carried out as described below.

(1) Materials:

Urease-gylcerol extract - this material should be refrigerated when not in use. The activity should be checked periodically using standard urea solutions.

Acetate buffer - 15 gms of sodium acetate are dissolved in 30 c.c. of H_2O, 10 ml. of glacial acetic acid added and then sufficient water to yield 100 ml. of solution.

Indophenol test solution #1 - to 10.0 gms of phenol

and 0.050 gms of sodium nitroprusside are added sufficient H_2O to make 1 liter. Store in an amber bottle and refrigerate.

Indophenol test solution #2 - to 5.0 gms of sodium hydroxide and 8.0 gms of commercial (5.25%) bleach (sodium hypochlorite) is added sufficient water to make 1 liter. This reagent likewise is stored in an amber bottle and refrigerated when not in use.

Standard urea solutions - 1.763 gms of dry urea (dried at 100°C) are dissolved in 1 liter of water. (This solution contains the equivalent of 1000 mgs. of NH_3 per liter and is used in dilutions of 2/1000 and 5/1000 for the daily indophenol calibration curve.)

(2) Dilution of Sample:

1/2 ml. aliquot of urea sample solution is diluted to 1 liter with de-ionized water.

(3) Conversion to Ammonia:

1 ml. aliquots of the diluted sample and standards are carefully pipetted into 10 ml. volumetric flasks. To the aliquots are added 1 drop of urease and 2 drops of acetate buffer. The flasks are carefully rotated to insure complete mixing of the reagents and then allowed to stand for 30 minutes. (The diluted standard urea solutions are used as standards for each analytical series.)

(4) Conversion to Indophenol:

At the end of the afore-mentioned 30-minute period, 4 ml. each of Indophenol test solution #1 and #2 are pipetted into the 10 ml. volumetric flasks followed by sufficient H_2O to bring to the 10 ml. mark. The solutions are allowed to stand a minimum of 30 minutes, poured into the "Spectronic 20" test tube and the optical density measured against a blank consisting of all the additives but the urea. After an additional 15 to 30 minutes the O.D.'s are again read versus the blank to insure that all the colors are completely developed.

(5) Calculation:

A plot of [urea] vs. optical density is made and from the slope ([urea] per O.D. unit) the concentration of the urea in the diluted aliquots is calculated. These figures are then multiplied by the dilution factor to arrive at the concentration of urea in a given sample.

I. Electrical Resistance in 40% KOH

The resistances of the samples are measured in the cell as shown in Figure 6, whose circuitry is shown in Figure 7.

The resistance of the cell without the film, immersed in 40% KOH, is determined. The resistance of the cell with the film in place is then determined after allowing 30 minutes for the film to equilibrate. Since the platinized platinum electrodes are one inch by one inch, the

resistance of the sample in milliohms/in^2 is given by the difference in the cell readings with and without the film in place.

2.2 Results Obtained to Date

The test results obtained to date are given in tabular form on the following pages.

Sample	Exchange Capacity	% Graft	Grafted units 1000 polymer units
2.1H	4.2 meq/gm	43.0	165
2.1L	3.3 meq/gm	31.0	120
5.1H	3.2 meq/gm	30.0	415

			Dimensional Changes		
Sample	Resistance	Thickness	L %	W %	T %
2.1H	20 $m\Omega$ - in^2	1.5 mils	7.0	9.5	0.0*
2.1L	35 $m\Omega$ - in^2	1.5 mils	4.5	6.0	0.0*
5.1H	15 $m\Omega$ - in^2	1.5 mils	7.5	5.5	0.0*
4.1H	25 $m\Omega$ - in^2	1.5 mils	5.5	9.0	
2.3HX	50 $m\Omega$ - in^2	1.5 mils	6.0	8.0	0.0
4.3HX	30 $m\Omega$ - in^2	1.0 mils	6.5	8.8	0.0

* No change in thickness detectable.

Sample	Number of 2-hour Cycles	Visual Check and Comments
Cellophane PUDO-300	6	Shorted out, heavily silvered. Dry resistance, 50 ohms.
2.1H	100	Samples show silver or silver-oxide deposits around edges of the surfaces contacted by the electrodes.
2.1L	100	Samples are easily pinholed by slight protuberance on the electrode surface. Several samples were used before a pinhole free run was obtained. Samples are slightly discolored and show silver-oxide deposits around edges of electrode contacted surfaces.

III. Summary

It has been shown that the process variables do allow a degree of control over the membrane parameters measured to date. There is as yet insufficient data to determine either the precision of this control of parameters or the importance of these parameters on the performance of the membranes in actual silver oxide-zinc cell operation.

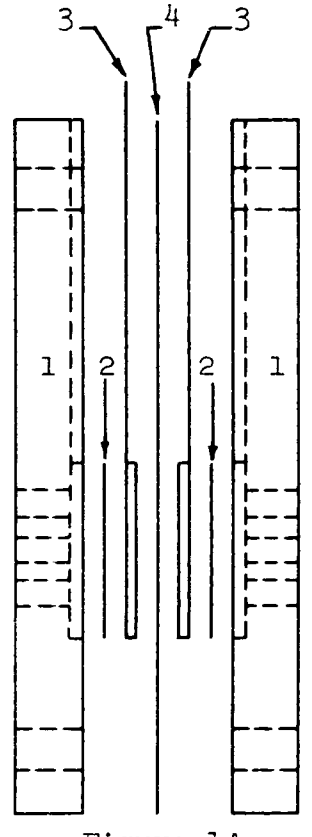


Figure 1A
Oxidation Cell Test

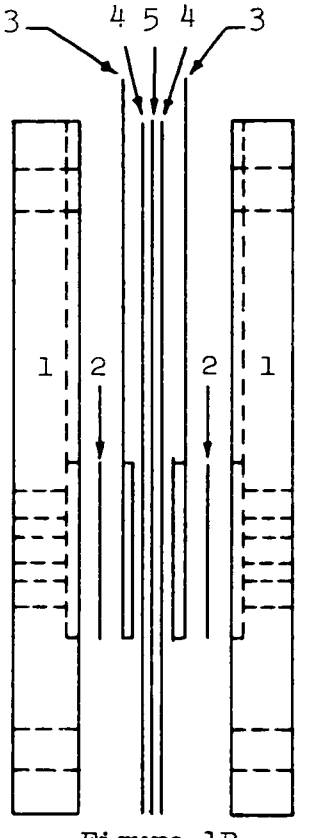


Figure 1B
Silver "Loading" Test

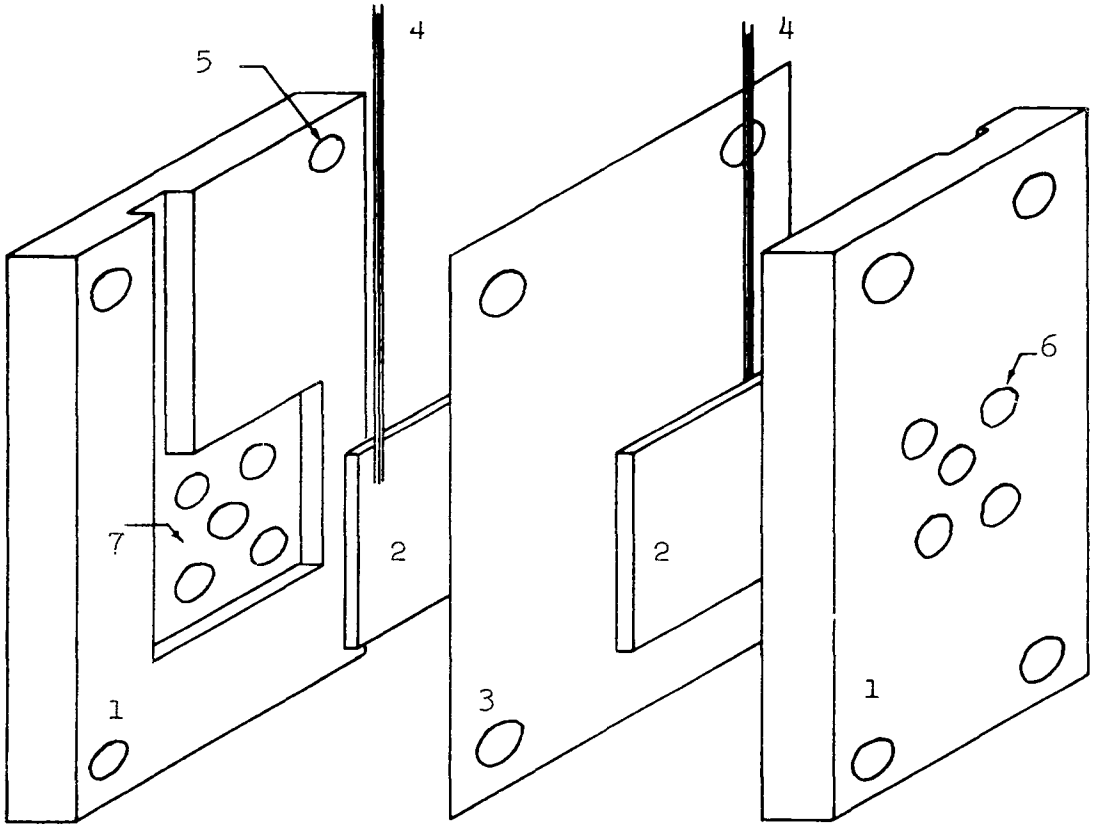
LEGEND

fig 1A

1. Clamping Plates
2. Porous Absorbents
3. Silver Electrodes
4. Membrane Under Test

fig 1B

1. Clamping Plates
2. Porous Absorbents
3. Silver Electrodes
4. Membrane Under Test
5. Cellophane

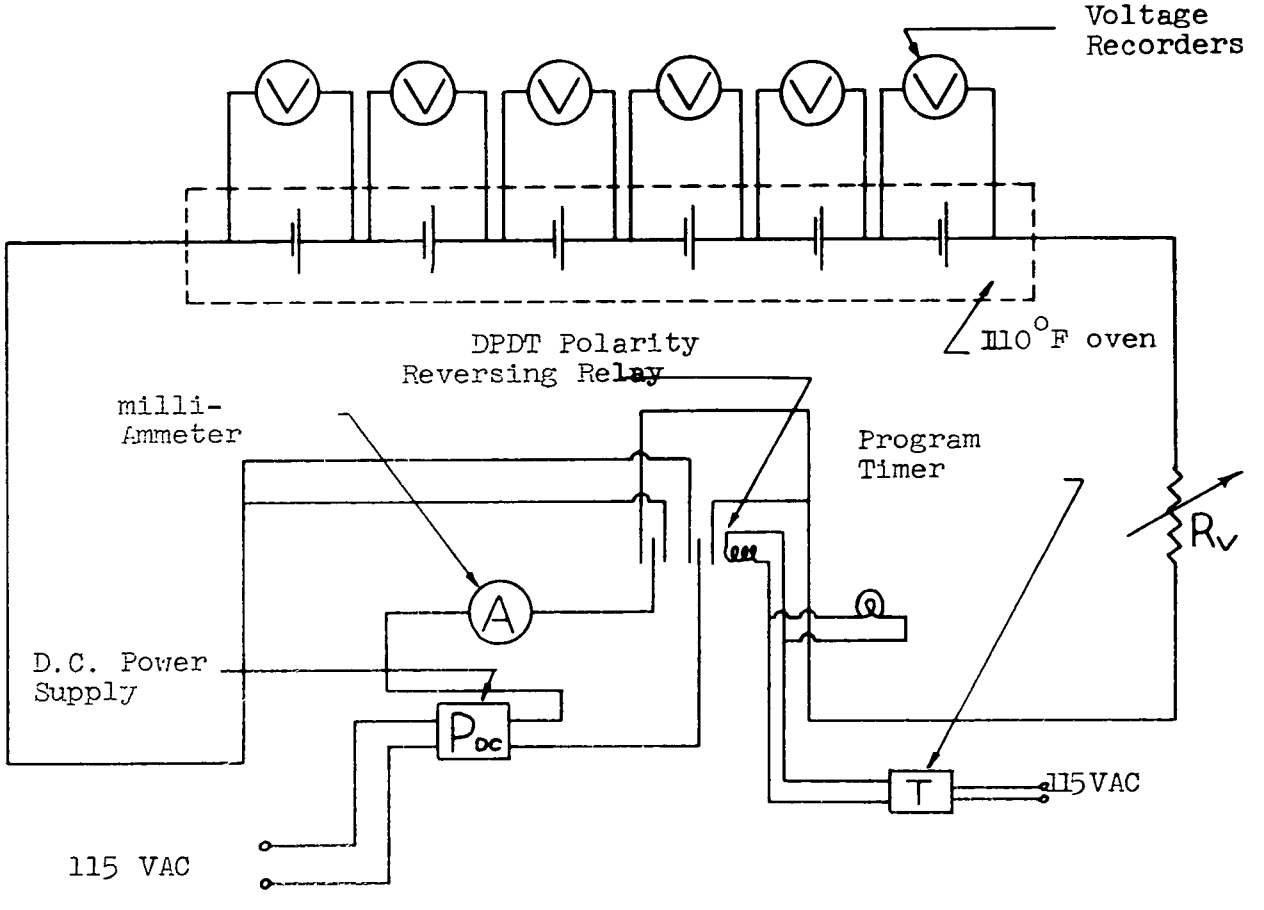


LEGEND

1. Clamping Plates
2. Silver Electrodes
3. Membrane Under Test
4. Leads to Cycling Equipment
5. Holes for Stainless steel Bolts
6. Perforations
7. Machined Depressions

Oxidation and Silver "Loading" Test Cell
Exploded View

Figure 2



Circuit Diagram of Cell Cycling Equipment
Figure 3

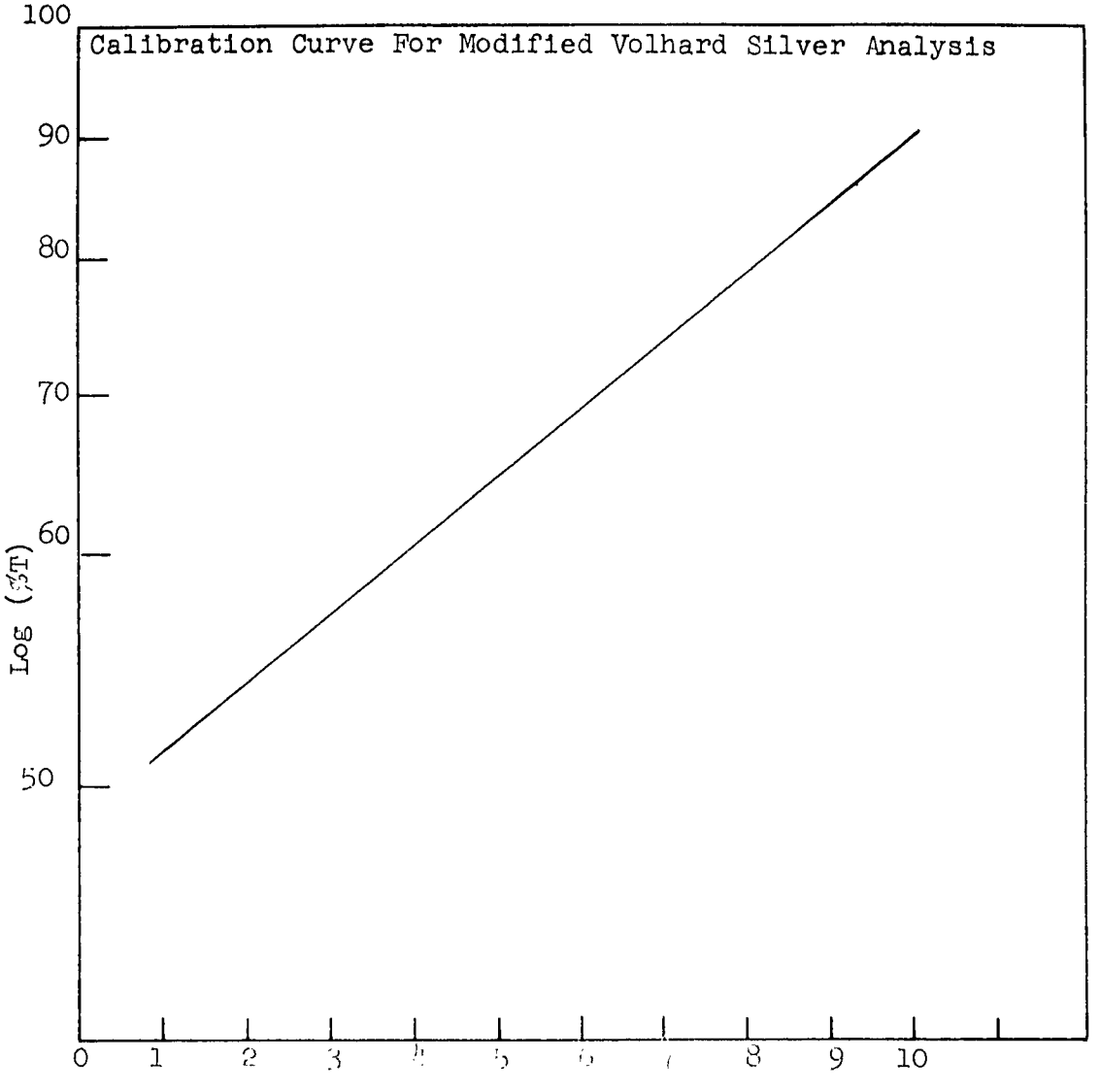
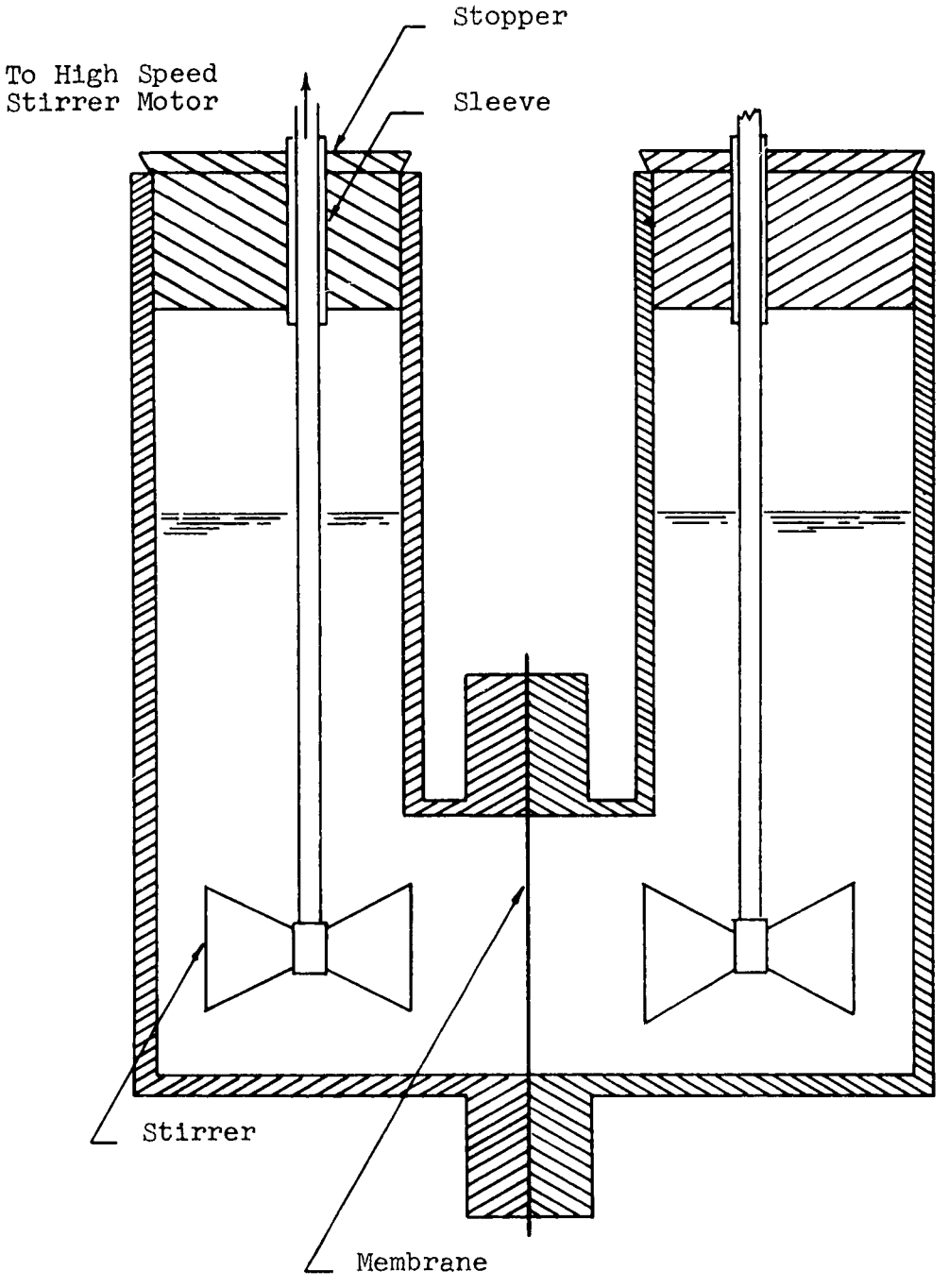
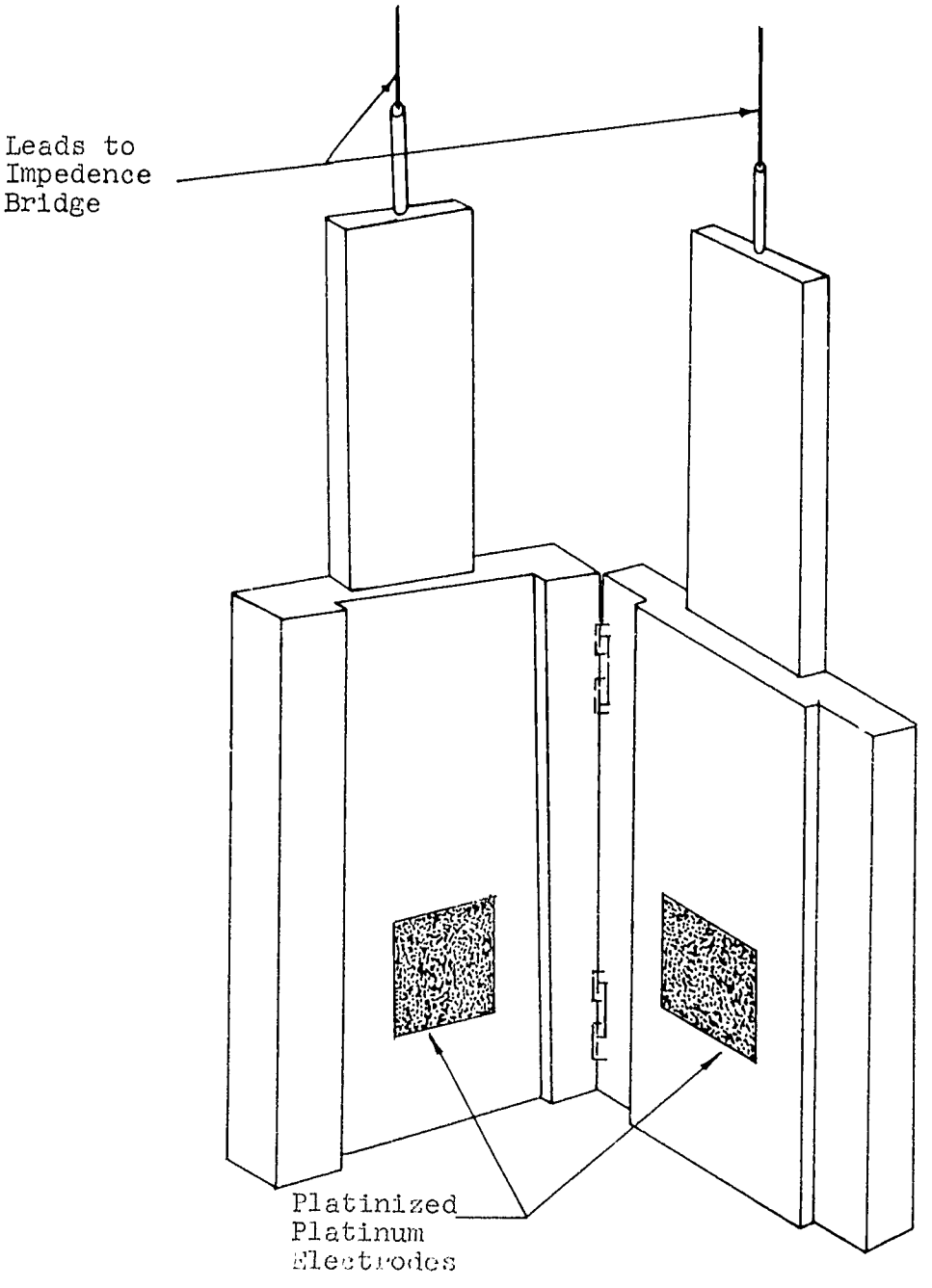

Calibration Curve For Modified Volhard Silver Analysis
100
90
80
70
60
50
Log (%T)
0
1
2
3
4
5
6
7
8
9
10
milligrams of silver/100 ml solution

Figure 4

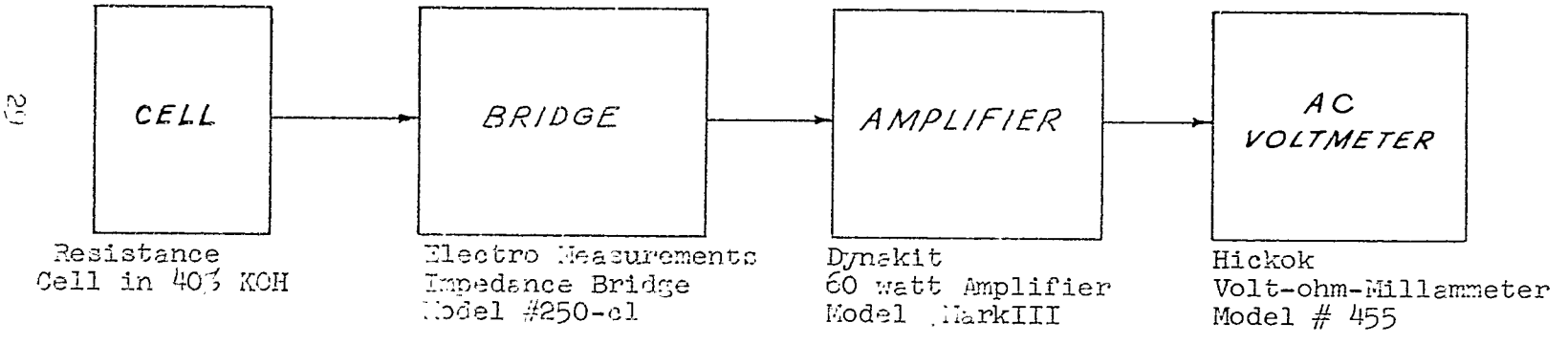


Cross Section of Dialysis Cell
Figure 5



Resistance Cell
(in open position)

Figure 6



Membrane Resistance Measurement Apparatus

Figure 7

Distribution List

Cys	Activities at WPAFB
1	ASAPT
1	ASAPRL (Library)
1	ASEP
2	ASRMA
1	ASRMOO
5	ASR PP-20

Other Dept of Defense Activities

Army

1 Dr. Adolf Fischback (Chairman)
Special Purpose Battery Branch
Power Sources Division
U.S. Army Signal R&D Laboratory
ATTN: SIGRA/SL-PSS
Fort Monmouth, New Jersey

1 OASD (R&E), Rm 3E-1065
The Pentagon
ATTN: Technical Library
Washington 25, D. C.

1 Commanding Officer
Diamond Ordnance Fuze Laboratory
ATTN: Library Rm 211, Bldg. 92
Washington 25, D. C.

1 U.S. Army Signal R&D Laboratory
ATTN: Mr. P. Rappaport
Fort Monmouth, New Jersey

1 Mr. E. F. Cogswell
Electrical Power Branch
Engineering R&D Laboratory
Fort Belvoir, Virginia

Navy

1 Mr. P. Cole
Naval Ordnance Laboratory
(Code WB)
Silver Spring, Maryland

Navy

1 Mr. W. H. Fox
Office of Naval Research
(Code 425)
Department of the Navy
Washington 25, D. C.

Air Force

1 AFCRL (CRZK, Mr. Doherty)
L G Hanscom Fld
Bedford, Mass.

1 SSD (SSTRE, Maj. Iller)
AF Unit Post Office
Los Angeles 45, Calif.

10 ASTIA
Arlington Hall Stn
Arlington 12, Va.

National Aeronautics and Space Administration

2 NASA
Lewis Research Center
ATTN: Dr. Louis Rosenblum
2100 Brookpark Road
Cleveland 35, Ohio

1 NASA
Marshall Space Flight Center
ATTN: M-G & C-EC,
Mr. E. H. Cagle
Bldg. 4487 - Guidance & Control
Huntsville, Alabama

Non Government

1 Calvin College
Department of Chemistry
ATTN: T. P. Dirkse
Grand Rapids, Michigan

1 Power Sources Division
Telecomputing Corporation

3850 Olive Street
Denver, Colorado

IV. Distribution List (Continued)

Cys	Non-Government (Contd)
1	Gulton Industries, Inc. Alkaline Battery Division ATTN: R. C. Shair 212 Durham Avenue Metuchen, New Jersey
1	Dr. Arthur Fleischer, Consultant 466 South Center Street Orange, New Jersey
1	P. R. Mallory & Company ATTN: Mr. R. E. Ralston 3029 E. Washington Street Indianapolis 6, Indiana
1	Lockheed Missiles & Space Company ATTN: J. E. Chilton Sunnyvale, California