

UNCLASSIFIED

Westinghouse Research Report 66-1B6-BSEPA-R1

SEPARATOR DEVELOPMENT FOR A HEAT STERILIZABLE BATTERY

A. Langer
R. G. Charles
C. R. Ruffing

GPO PRICE \$ _____

CFSTI PRICE(S) \$ _____

September 30, 1966

Hard copy (HC) 2.00

Microfiche (MF) .50

Contract No. 951525

ff 653 July 65

"This work was performed for the Jet Propulsion Laboratory,
California Institute of Technology, sponsored by the National
Aeronautics and Space Administration under Contract NAS7-100."

Westinghouse Electric Corporation
Research Laboratories
Pittsburgh, Pennsylvania 15235

First Quarterly Report

Period: June 1, 1966 to September 30, 1966

N67 13212
(ACCESSION NUMBER)
30 (PAGES)
AL 80529
(NASA CR OR TMX OR AD NUMBER)
(THRU)
(CODE)
03
(CATEGORY)

FACILITY FORM 602

Approved: W. T. Lindsay, Jr.

W. T. Lindsay, Jr., Manager
Physical Chemistry R&D
Westinghouse Research Laboratories

Approved: J. Swiss

J. Swiss, Director
Chemical Sciences R&D
Westinghouse Research
Laboratories

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

SEPARATOR DEVELOPMENT FOR A HEAT STERILIZABLE BATTERY

First Quarterly Report

A. Langer
R. G. Charles
C. R. Ruffing

Westinghouse Research Laboratories
Pittsburgh, Pennsylvania 15235

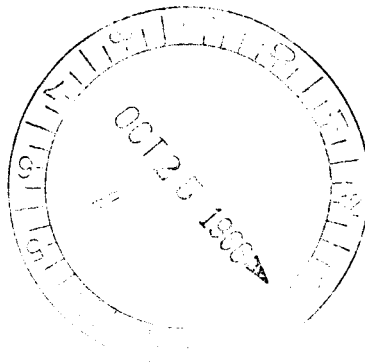
JPL Contract No. 951525

Abstract

13212

Two approaches are being pursued in attempts to produce separators for silver-zinc cells that must be subjected to sterilization heat treatment. The major effort is on preparation and characterization of composite separators, containing inorganic materials within a porous matrix of organic material. Several filler and matrix materials have been identified as promising components by screening tests of many candidate materials for KOH resistance. Experimental composites have been prepared by impregnation. These are being characterized by measurement of electrolytic conductivity, electrolyte diffusion rate, silver and zinc diffusion rates, resistance to dendrite penetration, and mechanical measurements. Instruments are described for carrying out the conductivity and diffusion rate measurements. The results are not yet conclusive; however, it appears that conductivity requirements of battery separators are initially met or exceeded by several of the experimental composites. Additional measurements are required after subjecting the separators to heat cycles.

REVIEWED CAS	
Contract Analyst	☐
10/6 RH	<i>RH</i>



A secondary effort is aimed at bonding of chelating functional groups to a porous organic structure. The approach has been to incorporate 8-hydroxyquinoline into epoxy resins through the use of Mannich bases as hardeners. Work so far has been devoted to synthesis of the Mannich base intermediates.

HEAT STERILIZABLE BATTERY SEPARATORS

First Quarterly Report

A. Langer, R. G. Charles, C. R. Ruffing
Westinghouse Research Laboratories
Pittsburgh, Pennsylvania 15235

1. INTRODUCTION

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 be flexible and must be free from imperfections, such as pinholes and cracks. At the same time the total thickness should not exceed 6 mils. Multiple wraps of thinner membranes are preferable.

This project is an exploratory study of composite separators that may possibly perform the above functions and possess the desired properties. We intend 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 is 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 will be devoted to modification of macroporous and microporous organic matrices by attachment of chelating functional groups.

Composite separators will be prepared by a variety of fabrication procedures. These experimental separators will then 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 will be made only on selected membranes.

Progress during the period covered by this report has been in the following areas: (a) qualification of organic matrix and inorganic filler materials for resistance to hot 40% KOH; (b) fabrication of experimental separators; (c) development of techniques for membrane characterization; (d) characterization of experimentally fabricated separators; and (e) synthesis of resins with bonded chelating functional groups. Details of progress are given in the following sections of the report.

2. ORGANIC SUBSTRATES

A large number of polymeric materials have been 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
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 hrs. The cooled, washed and dried samples were reweighed and measured. Representative data are given in Table I.

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 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 ZrO_2 , TiO_2 , SnO_2 , ThO_2 , MgO , as well as the molecular sieves Linde 4A and 5A are relatively insoluble. Molecular sieve 13A is probably borderline, with 92.3% remaining undissolved. The weight gains observed for TiO_2 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 hrs. 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 ZrO_2 remains undissolved at 135°C. For barium zirconate 82.6% remained undissolved under the same conditions.

4. SEPARATOR 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. (In some instances a sandwich construction was used. Two separate squares of support material were pressed together after coating, while still wet, and then dried.)

5. TEST EQUIPMENT FOR STUDYING MEMBRANE CHARACTERISTICS

5.1. 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 are being 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 Fig. 1.

A closed system is employed for filling and emptying the cell without exposing the concentrated KOH solution to air. Separate leveling bulbs were used for each compartment to prevent any possible cross-leakage of current. Large external Hg-HgO reference electrodes were prepared from purified HgO by grinding with mercury metal. The resulting mixture was placed on top of a mercury pool. The electrolyte in the reference cells was 40% KOH. Connection between the half cells and the liquid in the measuring cell was made by means of asbestos twine soaked in the electrolyte and contained in a polyethylene tube. The twine protruded from the ends of the tube. This precaution prevents formation of air bubbles in the bridge, eliminating a high resistance path.

* 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 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. The resistance is calculated from the potential difference between the two reference electrodes.

5.2. 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, Yardley, Pennsylvania, with the exception that here also a closed system was adopted to eliminate the need for filling of the cell with fresh electrolyte for each test. The platinum wires used as sensing electrodes are very close together and separated only by a thin Teflon film glued to the surface of the Lucite container. The Teflon facing has the advantage in that it retards leaking of electrolyte from the membranes during testing. The area of membrane exposed for measurement is 0.25 in. diameter. In order to test larger membranes at different spots, the recommended dowl pins for alignment were replaced with sliding bars outside the container. This cell is used in conjunction with a Wayner-Kerr bridge, using a low impedance adaptor. A photograph of the apparatus for this determination is shown as Fig. 2.

5.3. 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.

Since the polarographic zincate determination can be made with relative ease and with sufficient accuracy over a wide range of concentrations, an instrument was constructed which included the mercury dropping electrode as the sensing element. The construction is shown schematically in Fig. 3.

The diffusion cell consists of two vessels machined from Lucite rods, with the aperture placed between flat parallel surfaces. In this way, no appreciable dead volume can develop around the membrane which would not be stirred by the magnetic stirrers. The flat portions also more efficiently prevent leakage of electrolyte around the membrane. The vessels are inserted into a stainless steel frame, giving excellent alignment without the use of dowl pins. Fig. 4 is a photograph of this apparatus.

It was necessary to record the whole zincate wave in order to evaluate the diffusion current. Therefore, the mercury dropping electrode is not in the diffusion compartment. The electrolyte is transferred at various time intervals into a small compartment by means of a rubber suction bulb. The small vessel contains the mercury dropping electrode and also has the nonpolarizable Hg/HgO electrode connected to the vessel by a bridge. By proper connections, all parts of the arrangement can be kept under nitrogen. The diffusion time is now the elapsed time until the electrolyte is drawn into the vessel. The electrolyte is returned to the vessel after the polarogram is taken so that no dilution error results.

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 well-defined polarographic wave can be obtained at the higher concentrations of the zincate.

A linear relation exists between the diffusion current and the zinc concentration in concentrated KOH. However, an unexpected phenomenon was observed, namely a dependence of the diffusion current on the potassium hydroxide concentration. If the polarograms are taken with the same concentration of zinc in solution, but with the supporting electrolyte at different concentrations, the relation shown in Fig. 5 is obtained, indicating that the diffusion current diminishes with higher concentrations of the supporting electrolyte. This decrease is relatively large and might reflect a change in the diffusion coefficient of the zincate ion or a change in the nature of the diffusing species.

5.4. Electrolyte diffusion through separator membranes

Electrolyte diffusion through a separator should be connected to some extent with its electrical resistance. The additional parameter thus obtained (an effective diffusion coefficient) characterizes the permeability to the OH^- and K^+ ions. 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. Such measurements can be performed with relative ease. Consequently, most of the membranes prepared were tested for electrolyte diffusion. This was done first for quality control purposes as membranes were prepared, and later, more carefully, for characterization of some of the membranes.

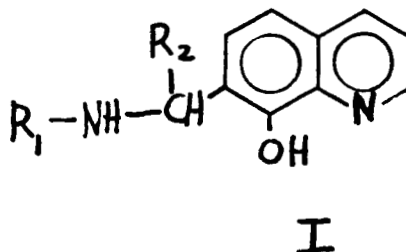
The procedure adopted for electrolyte diffusion measurements consists of straightforward recording of OH^- ion concentration increase by pH measurements of initially pure water on one side of the membrane, with 40% KOH on the other side. Taking into account the parameters of the apparatus, the diffusion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

6. RESULTS OF MEMBRANE CHARACTERIZATION MEASUREMENTS

Table IV contains the results so far available on measurements of electrical resistivity and electrolyte diffusion through experimental separators. Measurements of zincate diffusion and dendrite penetration have not yet been conducted in a routine manner for characterization purposes. The most significant information indicated by the results of Table IV is that many of the experimental composites do have acceptably low values of resistivity. More complete evaluation of the membranes must await additional characterization measurements, both before and after sterilization heat treatment.

7. RESINS CONTAINING BONDED CHELATING GROUPS

The general approach emphasized in this phase of the work has been the incorporation of 8-hydroxyquinoline chelating groups into epoxy resin matrices. Work during the first quarter has been restricted largely to the preparation of the intermediate Mannich bases I.



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

The compounds I are prepared from the interaction of the aldehyde R_2CHO , the amine R_1NH_2 and 8-hydroxyquinoline in alcoholic solution, employing prolonged reaction periods. Table V lists the compounds so far prepared together with some of the preparative details. Preliminary experiments indicate that the assumption made above, that the molecules I can be linked into the epoxy resin structure through the secondary amino groups, is justified.

A. Langer

A. Langer
Physical Chemistry R&D

R. G. Charles

R. G. Charles
Physical Chemistry R&D

C. R. Ruffing

C. R. Ruffing
Insulation & Chemical Technology

Table I

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

Sample	% weight change		Dimension change (%)	
	RT	135°C	av. lgth. and width	thickness
<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
Afco 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)

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

Table II

Solubility of Inorganic Filler Materials

	<u>Solubility in 40% KOH at 25°C (grams/100 ml)</u>
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 Fabrication							
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 (b)	Drying Conditions	Weight (grams)	
							Uncoated	Coated
62-7-26-3	4.5	SW	Phenoxy Resin (Poron)	DMAC	Zr(OH) ₄	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 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 IV

Characteristics of Experimental Membranes at a Temperature of 25°C ± .5

Sample No.	Composition		Thickness (mils)	Resistivity (ohm/cm)	Electrolyte Diffusion Coefficient (10 ⁻⁸ cm ² /min)
	Base	Binder Filler			
	Cellophane		0.0030	73.7	-
30-6-29-1	Pellon	None ZrO	0.0251	8.2	-
30-6-30-1	Pellon	Polysulfone None	0.0427	105.4	-
30-6-29-2	Pellon	None None	0.0274	0.9	-
34-6-30-1	Pellon	Polysulfone ZrO	0.030	66.0	-
29-6-28-1	Teflon	Polysulfone ZrO	0.034	27.1	-
42-7-13-1	Pellon	Polysulfone ZrO	0.028	94.3	-
44-7-14-1	Pellon	None ZrO	0.028	12.8	-
50-7-18-1	Webril	Polysulfone ZrO	0.057	132.0	-
53-7-19-3	Webril	Polysulfone ZrO	0.029	3.6	-
53-7-20-1D	Webril	Polysulfone ZrO	0.012	1680.3	-
53-7-20-1F	Webril	Polysulfone None	0.006	1439.3	-
53-7-20-1C	Webril	Polysulfone ZrO	0.011	2122.8	-
56-7-21-2	Webril	Polyphenyl Oxide ZrO	0.005	201.2	-
57-7-22-1	Webril	Polyphenyl Oxide None	0.006	118.9	-

(Continued)

Table IV (Continued)

Sample No.	Composition			Thickness (mils)	Resistivity (ohm/cm)	Electrolyte Diffusion Coefficient (10^{-8} cm ² /min)
	Base	Binder	Filler			
56-7-21-3	Webril	Polyphenyl Oxide	ZrO	0.012	27.6	-
56-7-20-1	Webril	Polysulfone	ZrO	0.013	28.4	-
56-7-21-1	Webril	Polyphenyl Oxide	ZrO	0.010	1309.5	-
55-7-20-3	Webril	Kynar	ZrO	0.010	318.3	-
55-7-20-4	Webril	Kynar	ZrO	0.010	44.8	-
55-7-20-2	Webril	Polysulfone	None	0.010	1936.9	-
60-7-25-2	Webril	Kynar	ZrO	0.014	324.0	-
60-7-25-1	Webril	Kynar	ZrO	0.008	234.0	-
58-7-22-1	Webril	Kynar	ZrO	0.008	43.3	-
57-7-22-2	Webril	Polyphenyl Oxide	ZrO	0.009	97.4	-
57-7-22-3	Webril	Polysulfone	None	0.002	~ 500	-
Battery Cellophane	-	-	-	1.1	73.7	7.6
62-7-26-1	Webril	Poron	None	1.8	139.8	-
62-7-26-2	Webril	Poron	ZrO	2.5	1136.0	-
62-7-26-3	Webril	Poron	ZrO	4.1	210.0	-

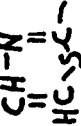
(Continued)

Table IV (Continued)

Sample No.	Composition			Thickness (mils)	Resistivity (ohm/cm)	Electrolyte Diffusion Coefficient (10^{-8} cm ² /min)
	Base	Binder	Filler			
29-8-10-1	Webril	Kynar	None	1.6	122.0	14.8
28-8-9-1	Webril	Poron	MgO	4.1	61.1	11.5
28-8-10-1	Webril	Poron	MgO	4.8	32.9	5.5
28-8-10-2	Webril	Poron	MgO	2.6	96.4	60.0
29-8-10-2	Webril	Kynar	MgO	4.0	60.1	4.6
30-8-10-1	Webril	Kynar	MgO	3.6	62.0	16.0
30-8-10-2	Webril	Kynar	MgO	2.2	63.8	-
25-8-8-1	Webril	Polysulfone	MgO	5.0	18.5	-
27-8-9-1	Webril	Polysulfone	MgO	3.2	51.4	443.0
27-8-9-2	Webril	Poron	None	2.0	504.0	-
31-8-10-1	Webril	Polysulfone	MgO	2.9	33.8	7.44
32-8-10-1	Webril	Polysulfone	MgO	2.6	70.3	18.0
31-8-10-2	Webril	Polysulfone	MgO	2.0	123.0	-
33-8-11-1	Webril	Poron	MgO	3.1	45.2	6.3
25-8-8-2	Webril	Polysulfone	MgO	3.1	58.9	10.7
26-8-8-1	Webril	Polysulfone	MgO	2.7	35.4	19.7
30-8-10-3	Webril	Polysulfone	None	1.5	503.0	249.0
86-8-18-2	Webril	Polysulfone	ZrO	4.0	188.0	-
86-8-18-1	Webril	Polysulfone	ZrO	7.0	144.0	-

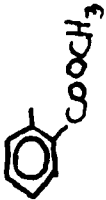
Table V

8-Hydroxyquinoline derivatives of structure I (see text)

Cmpd. No.	R ₁	R ₂	Reaction time (days)	Yield (%) crude	Yield (%) recryst.	Solvent system for recrystallization ^a
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 V (continued)

Ompd. No.	R_1	R_2	Reaction time (days)	Yield (%) crude	Yield (%) recryst.	Solvent system for recrystallization ^a
7		phenyl	31	40	--	---
8		phenyl	38	36	21	(A) 50 ml pyridine (B) 100 ml absolute ethanol
9		$\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-}$	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.

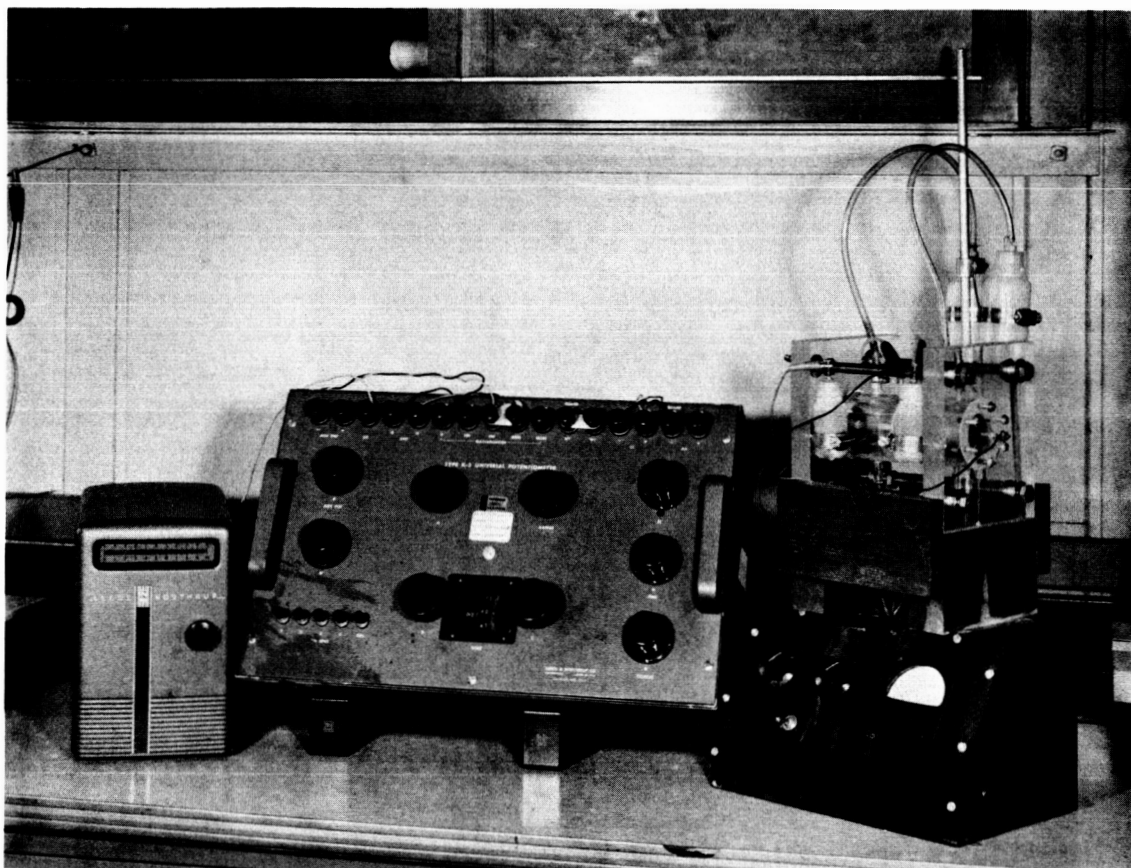


Figure 1. Resistivity tester - D.C. current method.

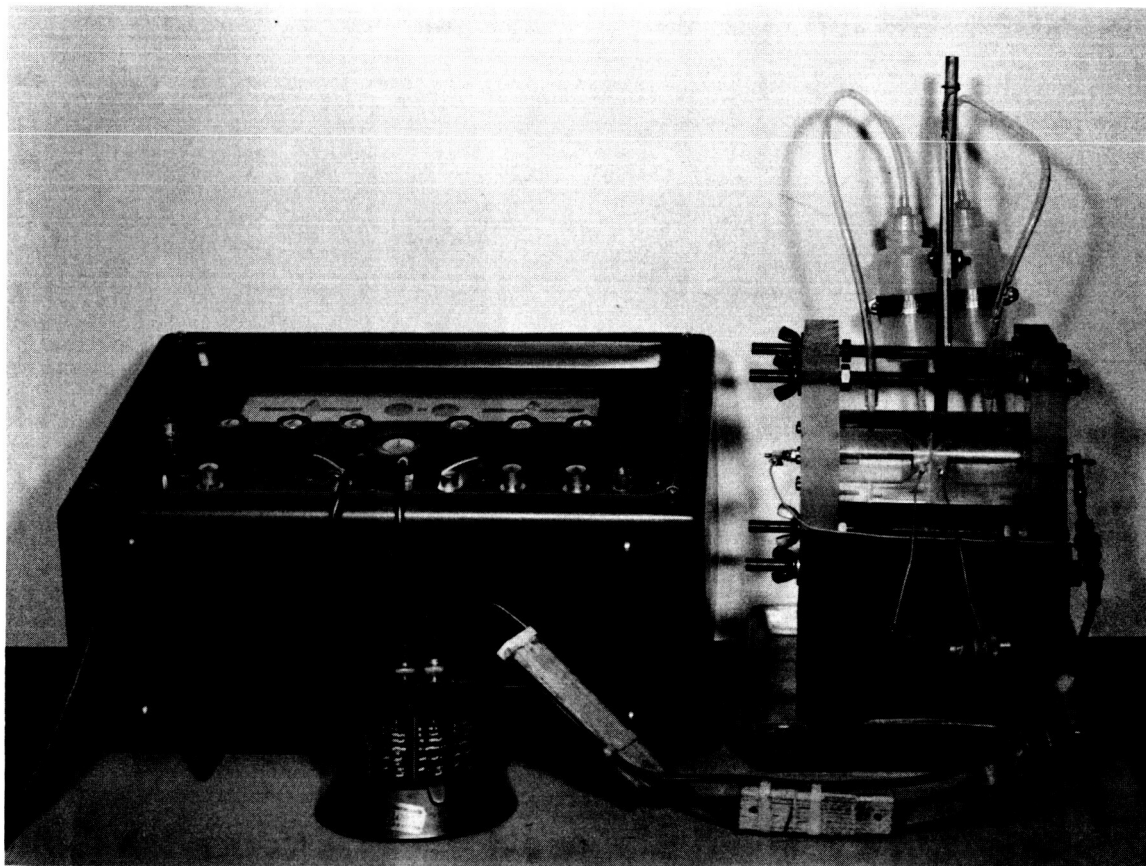


Figure 2. Resistivity tester - A.C. current method.

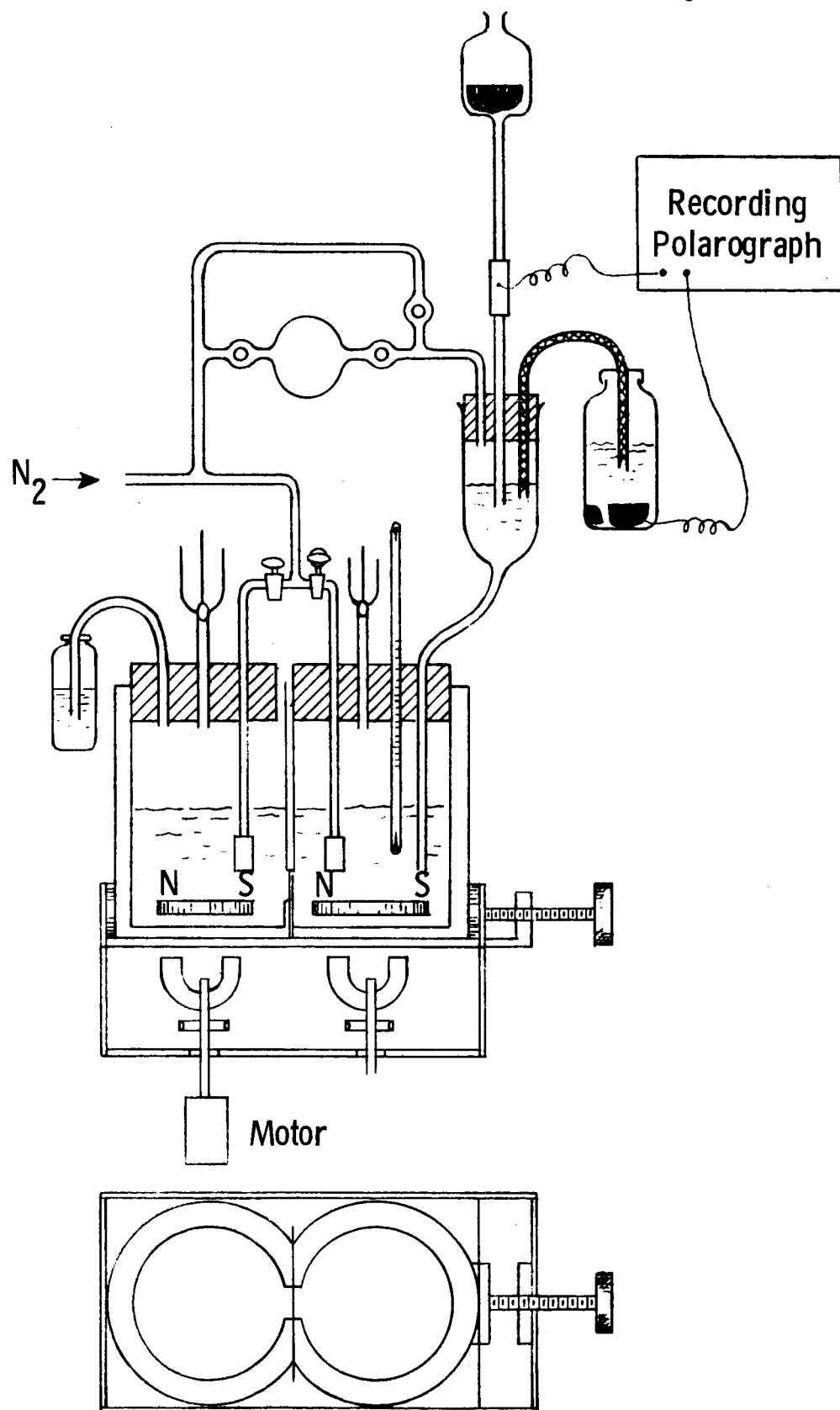


Fig. 3—Diffusion testing apparatus with polarographic sensing

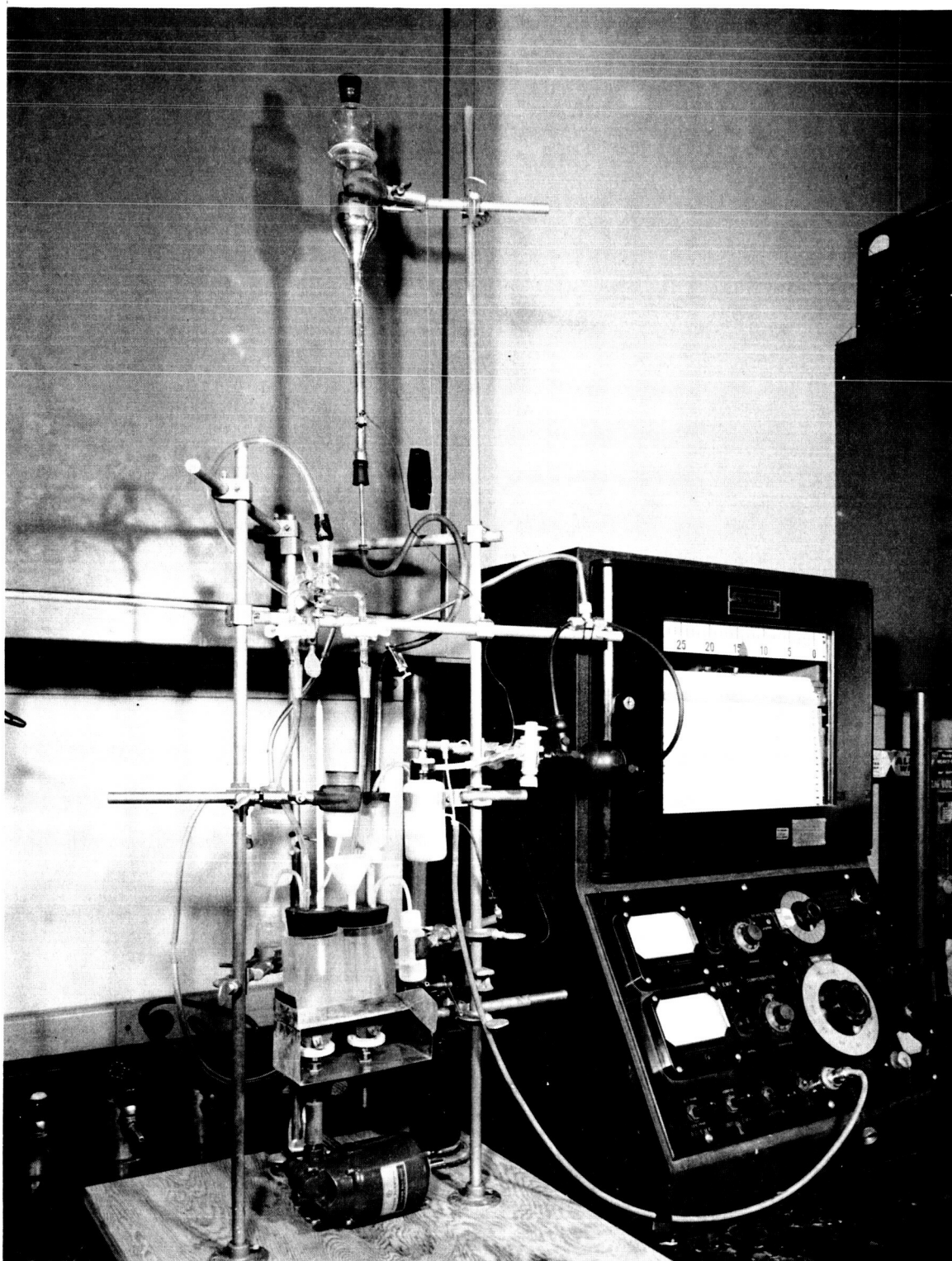


Figure 4. Instrument of diffusion measurement with polarographic sensing of Zn ion.

Curve 579046-A

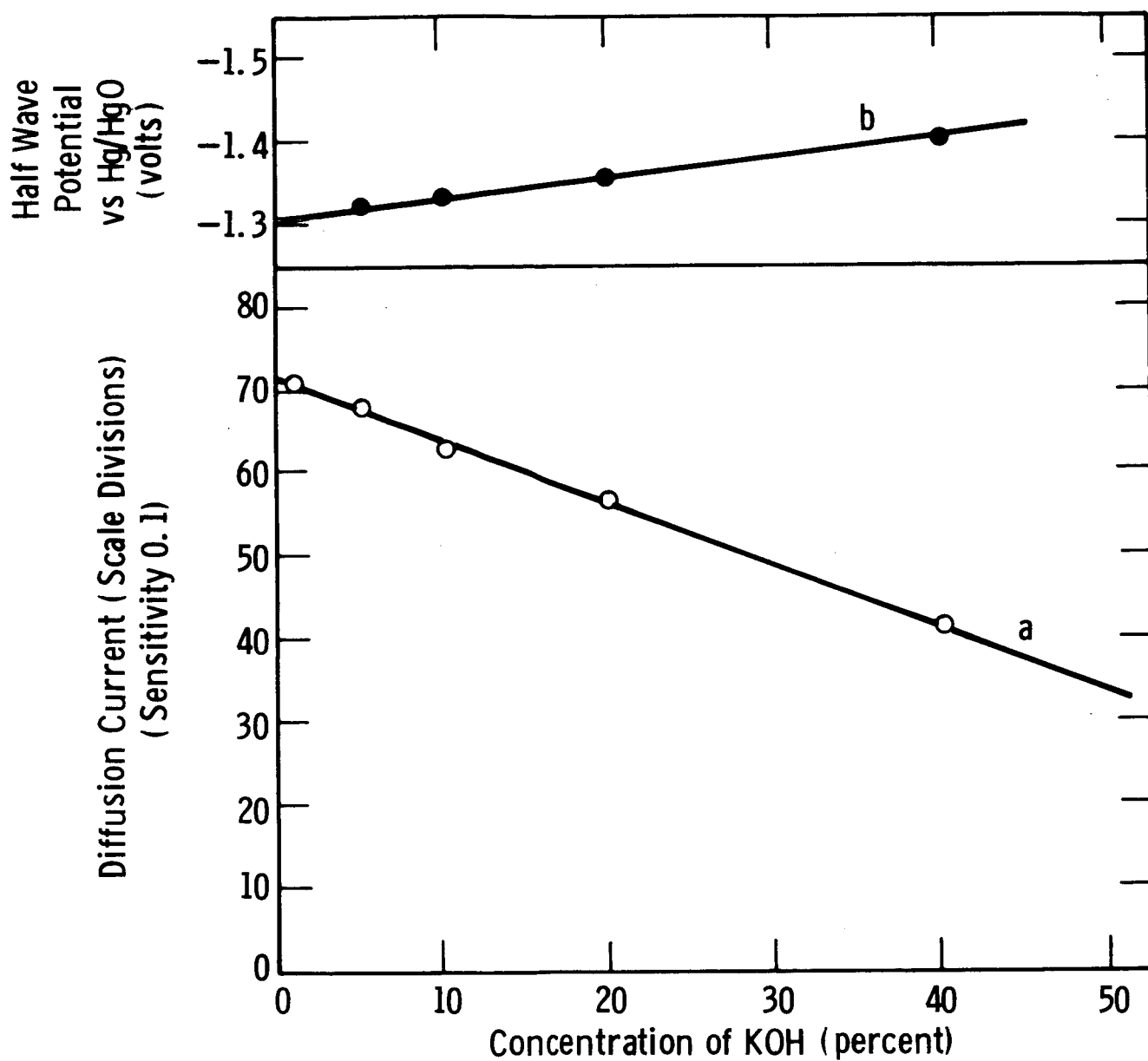


Fig. 5—Dependence of diffusion current and half wave potential of zincate ion on concentration of KOH