

DOE/NASA/0204-1
NASA CR-167872

NASA-CR-167872
19820022835

ANION PERMSELECTIVE MEMBRANE

Russell B. Hodgdon
Warren A. Waite

Ionics, Incorporated
Research Division
Watertown, Massachusetts 02172

LIBRARY COPY

AUG 26 1982

April 1982

LANGLEY RESEARCH CENTER
LIBRARY, NASA
HAMPTON, VIRGINIA

Prepared for
NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
Lewis Research Center
Cleveland, Ohio 44135
Under Contract DEN 3-204

for
U.S. DEPARTMENT OF ENERGY
Office of Advanced Conservation Technologies
Division of Energy Storage Systems
Washington, D.C. 20545
DE-AI-04-80-AL-12726



NF02687

NOTICE

This report was prepared to document work sponsored by the United States Government. Neither the United States nor its agent, the United States Department of Energy, nor any Federal employees, nor any of their contractors, subcontractors or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

To: NASA-LEWIS Research Center
Cleveland, Ohio 44135
Attn: Ms. J.S. Ling
MS 309-1

A Summary Report
Anion Permselective Membrane
DEN 3-204

Submitted by: Research Division
Ionics, Incorporated
65 Grove Street
Watertown, Massachusetts 02172
Tel: (617) 926-2500

Prepared by: Russell B. Hodgdon
Warren A. Waite

Approved:


Edgardo J. Parsi

Director of Research

N82-30711#

TABLE OF CONTENTS (Continued)

	<u>Page</u>
4.4-I CD1L-AA5 Type Helium Study-----	41
4.5-I CD1L-AA5 Type Optimization-Selectivity Study-----	43
5.0-I Exploratory Tests Woven Fabrics - Poly- propylene - CD1L-AA5 LC-Multifilament Warp & Spun Filling-----	47
5.0-II Exploratory Tests Non-woven Fabrics - Polypropylene Random Fiber Orientation - CD1L-AA5-LC-----	50
5.0-III Woven Polypropylene-CD1L-AA5-LC-----	52
5.0-IV CD1L-AA5-LC Non-woven Polypropylene - Ply Study-----	53
5.0-V CD1L-AA5-LC Melt Blown Polypropylene-----	55
5.0-VI CD1L-AA5-LC Non-woven Polyethylene-----	58
5.0-VII CD1L-AA5-LC LC Type Wetting Study-----	61

FOREWORD

This document constitutes the final report for the work accomplished between November 1980 and April 1982 by Ionics, Incorporated, for the National Aeronautics and Space Administration, Lewis Research Center, under Contract DEN 3-204 entitled Development and Preparation of Redox Cell Anion Exchange Membranes.

Dr. Russell B. Hodgdon provided overall program management. The principal investigator was Warren A. Waite with major contributions from R.B. Hodgdon, A. Scieszko, M. Thomas, and C.H. Swenson.

Thanks are due to Dorothy Howard for her patience in typing the final report manuscript and its many revisions.

ABSTRACT

This report covers work on the synthesis and fabrication of polymeric anion permselective membranes for redox systems. Under the synthesis section variations of the prime candidate anion membrane formulation to achieve better resistance and/or lower permeability were explored. Under the fabrication section processing parameters were evaluated to lower cost and fabricate larger sizes.

The processing techniques to produce more membranes per batch were successfully integrated with the fabrication of larger membranes. Membranes of about 42" x 20" (107 cm x 51 cm) were made in excellent yield.

Several measurements were made on the larger sample 42" x 20" membranes shipped to NASA-Lewis. Among the data developed were water transport and transference numbers for these prime candidate membranes at 24°C. Other work done on this system included characterization of a number of specimens of candidate membranes which had been returned after service lives of up to sixteen months at the NASA Lewis Research Center.

The synthesis section includes work with new polymer constituents, the efforts with new N.P.'s, catalysts and backing fabrics. Some work was also done to evaluate other proportions of the ingredients of the prime candidate system.

The adoption of a flow selectivity test at elevated temperature was explored.

1.0 Introduction and Summary

Contract DEN 3-204, Development and Preparation of Redox Cell Anion Exchange Membranes represents a continuation of the efforts to synthesize, develop and evaluate anion perm-selective membranes to be used as cell separators in the redox energy storage system under development at the NASA-Lewis Research Center. Under previous contracts (NAS3-20108 and DEN 3-137) a number of candidate membranes of differing chemical properties had been synthesized, evaluated and the most promising one selected for further evaluation and testing.

This superior formulation then was adjusted as to monomer ratios, NP, and catalyst concentration to yield anion membranes of good redox cell efficiencies. The most promising membrane system, CD1L, was characterized, and processing methods developed to insure high yields of first quality anion membranes.

Under this contract, processing techniques were modified further to permit the scale up of CD1L membranes in the 42" x 20" size. The process gave good membranes and excellent yields.

Concurrently, a series of studies of NP variations, new fabrics, new monomer compositions (both type and proportion) and new catalysts were undertaken. This work was intended to initiate efforts to upgrade the performance of the system so

that ultimately redox membranes now capable of use for battery applications, may be adapted to use in utility load leveling systems.

The NP studies yielded a good alternate NP for the base CDLL system. The work with fabrics indicated non-woven fabrics to have characteristics which, with special techniques, could yield substantially lower thickness, lower resistance membranes with intriguing physical properties. Work with dichloroethylene (DCX) yielded membranes with good ion exchange capacities which need to be optimized by reducing their water content. The catalyst studies revealed one catalyst that had the capability of producing good quality CDLL type membranes at substantially lower cure temperatures allowing more latitude in the selection of NP solvents and the use of more temperature sensitive fabrics.

2.0 Summary of Results

In the first phase of this program a series of studies were undertaken to verify the performance of the prime candidate membrane and prove its system feasibility. The second phase, developmental in nature, consisted of a number of tasks undertaken to improve the efficiency of the anion exchange membranes thus permitting its application to additional areas of service.

The results of the studies on the prime candidate membrane system were:

- Tests on prime candidates membranes with up to 16 months battery service showed excellent retention of properties.
- Modifications of fabrication techniques were developed which reduced the cost of membrane production.
- Scale-up of prime candidate membrane to full 42" x 20" size was achieved with excellent yields.
- Transference and water transport numbers were measured on the prime candidate membrane at 25°C.

In the development area:

- Fabrication of DCX based membranes was initiated.
Current membranes have good resistivity but low selectivity.
- Membranes with high ratios of VBC content were found to form membranes with a high incidence of pinholes.
- A feasible low temperature catalyst was found; permitting consideration of temperature sensitive fabrics and more volatile NP's.

- Feasible alternate NP was found. N-Butanol appears to perform very well.
- A technique was developed for fabricating very thin membranes. Both single ply and laminated membranes were produced.
- Initiated elevated temperature ferric chloride fouling test program.

3.0 Improved Processing

Two modifications of the method of fabricating the prime candidate membrane system were evaluated under this phase of the program (Figure 1). Both were attempts to reduce the cost of the final product and speed production.

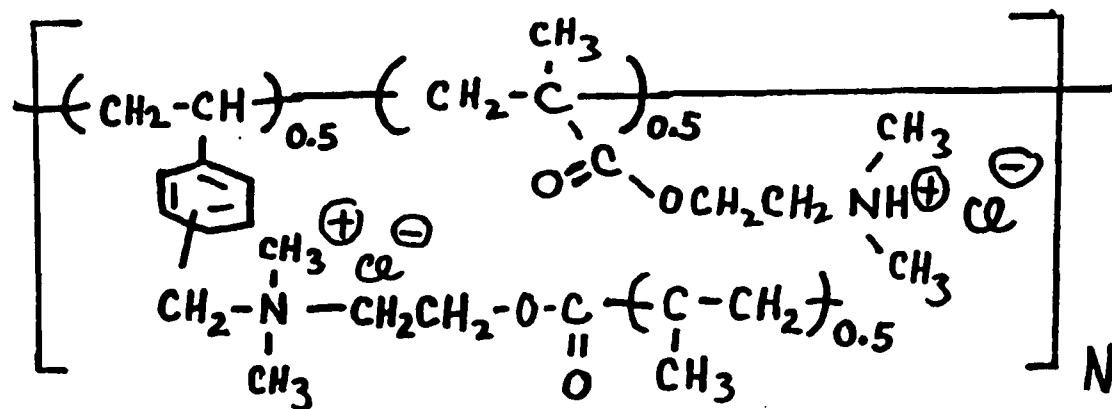
The first (W233-26) was a modification of the CD1L membrane laying technique to reduce waste and permit about an extra 30% more membranes to be produced per tray.

In another effort to achieve improved, more rapid processing the catalyst was predissolved in the VBC. This technique helps to minimize the time elapsed. This is the period when quaternization, with its undesirable viscosity build-up occurs after the DMAEMA is added and before the fabric immersion is completed.

The membranes produced by these techniques were fully characterized and appeared to be of good quality. (See table XYZ). When desirable these two techniques were subsequently used for membrane fabrication. (TABLE 3.0-1)

FIGURE I

PRESENT "REDOX" ANION EXCHANGE MEMBRANE SEPARATOR



1. ONE MOLE OF VINYL BENZYL CHLORIDE REACTS WITH ONE MOLE OF DIMETHYLAMINOETHYL-METHACRYLATE TO FORM AN IONIC DIMER.
2. IONIC DIMER REACTED WITH ONE MOLE OF DIMETHYLAMINOETHYL METHACRYLATE VIA FREE RADICAL POLYMERIZATION TO FORM IONIC POLYMER IN AND ABOUT FABRIC SHEET.

PROPERTIES: (TYPICAL)

A. THICKNESS = 0.040 cm.

B. RESISTIVITY
IN 0.1N HCL-1000 Hz. $\approx 4.2 \text{ OHM-CM}^2$

C. CAPACITY $\approx 4.2 \text{ MEQ/DGR}$

D. PERMEABILITY = $15 \text{ MGFe}^{+3}/\text{CM}^2\text{-HR-MOL}$

E. WATER CONTENT = 38 %

F. POLYMERIZED WITH 0.0625%
AIBN CATALYST.

TABLE 3.0-I
CDIL FABRICATION STUDY

<u>W233-</u>	<u>-26</u>	<u>-27</u>
Comment	More Membranes Per Tray	Premixed Catalyst
NP	.275	.275
Resistance 0.1N HCl (Ω -cm ²)	4.8	4.7
Thickness (cm)	.048	0.035
I.E.C. (meq/d.g.)	4.20	4.19
Strong	1.86	1.87
Weak	2.34	2.32
Water (%)	33.7	34.3

3.1 Membrane Scale-Up

One of the stated goals of the project was the preparation of the prime candidate membrane - CD1L - in the 42" x 20" size. The finished dimensions of these membranes would be between two and three times the area of any earlier membrane of the redox type.

Calculations were made that full batch requirements could be up to 18 liters in volume. Generally available trays, ovens etc., were judged adequate for this operation. Degassing, however, was a prime requirement and this required the procurement of a 22 liter three necked flask.

An initial process verification was made by checking out the equipment using eighteen liters of water. A standard laboratory vacuum pump readily pulled sufficient vacuum to boil the water (about 17 mm Hg at 20°C). The apparatus was subjected to several minor shocks to check its structural integrity. It withstood the treatment satisfactorily.

A small explosion-proof air motor secured for stirring or blending the batch was also evaluated. This appeared entirely adequate for the service involved.

The fabrication of these large membranes was made late in the program to allow selection of the most desirable formulation and permit the accumulation of more service life data. The prime formulation CD1L-AA5-LC (27.5% NP and 0.0625 catalyst) was selected for the membranes fabrication.

The 42" x 20" size was adopted to insure a final cut size of 18" x 40".

These membranes were prepared in a relatively straightforward scale up of normal fabrication procedures. The batch sizes tried were 10 and 12 liters. These were roughly double the largest previous batches but handled without undue difficulty. The weight of the monomer batch and the large sheets of glass used necessitated the use of two people, just about continuously, throughout the processing.

The first run was made with a 12 liter batch. No undue exotherm tendencies were noted during mixing, cooling or degassing. This run produced somewhat undercured membranes probably due to poor heat distribution in the four foot wide laboratory oven. None of the membranes exhibited any pinholes. Some of the membranes tended to stick to the edges.

A second run was made with a 10 liter batch. This time the tray was positioned higher in the oven. In addition to the oven monitors, thermocouples were placed in the edge resin and in one of the membranes. The time temperature profile was as programmed.

The resultant membranes appeared excellent in all respects and the yield was > 90%. The five 42" x 20" membranes shipped to the NASA-Lewis Redox Group were from this run. These membranes were fully characterized and the results listed below:

AA5-LC Formulation

Thickness	0.049 cm	Ion Exchange Capacity	
Resistance		Total	4.24 meq/dgr
in 0.1N HCl	4.9 Ω cm ²	Strong	1.80 " "
Water Content	35.1%	Weak	2.44 " "

Iron Selectivity Test
1M FeCl₃/0.5N HCl

Thickness	μ g Fe/hr/cm ²	M/L
0.046 cm	17.4	

From the results obtained and the experience gained in the processing of these large membranes it appears that most of the problems related to scaling up have been encountered and resolved. The problems which were solved in the production of 9" x 10" and the 18" x 18" membranes have enabled us to make the 42" x 20" with a minimum of difficulty. The major problems in the fabrication of these 42" x 20" have been in the mechanical handling of the heavier physical loads, the larger sizes of cloth and associated mechanical equipment. Basically no new chemical parameters were encountered. An outline of the process is found in Table 3.1-I.

TABLE 3.1-I
BASIC PROCESS SHEET

- A. Monomers & equipment cooled individually. (5°-10°C)

- B. Monomers & catalyst, combined and degassed with cooling (5-10°C)

- C. Membranes laid up, alternating fabric and interleaving.

- D. Membranes polymerized, cooled, removed from trays and characterized.

- E. Five 42 " x 20 " membranes shipped to NASA Redox Group.

This Page Intentionally Left Blank

TABLE 3.2-I

ANALYSIS OF MEMBRANES AFTER EXTENDED SERVICE

MEMBRANE TYPE	CDIL-AA5 (Low Cat 27.5 NP)		CDIL		CDIL-AA5		CDIL-AA5	
Service Area	From 40 cell pair stack		From 9" x 10" stack		From 9" x 10" stack Working Cell (16 mos)		From 9" x 10" stack Open Voltage Cell (16 mos)	
Date of Anal.	Jan, 1981		Dec, 1981		March, 1982		March, 1982	
Condition As Received	Generally Good appearance		Good-light Vermillion color		Generally Good appearance **		Generally Good appearance **	
Fluid Wash	pH 1		pH 1		pH 1		pH 1	
Fe test	positive		positive		positive		--	
<u>Properties</u>	<u>Flow Path</u>		<u>Flow Path</u>		<u>Flow Path</u>		<u>Flow Path</u>	
	<u>Edge</u>		<u>Edge</u>					
<u>Leak Test</u>	OK		OK		OK		OK	
<u>Thickness</u> cm	0.041		0.042		0.042		0.042	
<u>Resistance</u> in 0.1N HCl (Ω -cm ²)	4.6		4.7		4.9		4.9	
<u>Water</u> (bg wt)	37.0%		37.4%		35.3%		35.8%	
<u>Ion Exchg. Cap.*</u>								
Total	4.28		4.42		4.09		4.15	
Strong	1.83		2.22		2.24		2.13	
Weak	2.45		2.20		1.85		2.02	

* Milliequivalents per gram of dry resin

** Edge area too narrow to allow meaningful samples to be cut from edge area

3.3 Transport and Transference Numbers

As part of the continuing effort to define and characterize the prime redox membrane, measurements of water transport and transference numbers were made.

A series of runs was undertaken with a standard CD1L-AA5-LC membrane. This prime candidate membranes has been formulated at 27.5% NP and 0.0625 parts catalyst. Its physical properties were measured and the complete characterization is listed below:

Reference: W233-61

Thickness (cm)	Resistance 0.1N HCl $\Omega\text{-cm}^2$	Ion-exchange Capacity			Water	
		Total	Strong	Weak	(%)	Cloth
0.042	4.6	4.02	1.96	2.06	36.4	Calendered Mod-acrylic

These values were considered within the normal range for this anion exchange membrane and its water transport number was determined with 0.6N hydrochloric acid on both sides of the membrane. The determined value at 24.5C was 71 ml/Faraday, indicating a relatively tight, impervious membrane.

The transference number was also determined on this membrane and at this temperature. The solutions used were 1.20N HCl on one side of the membrane and 0.62N HCl on the other. The test cell was maintained at 24.5°C.

The transference number, T^- of this prime candidate membrane (CD1L-AA5-LC) was found to be 0.64.

This means 64% of the current is being carried by the Cl^- counter ion 36% is being carried by the invading H_3O^+ .

4.0 High Vinylbenzylchloride Content Membranes

The standard ratio of the CDLL formulation is two moles of DMAEMA to one of the VBC. This results in a chain with one mole of VBC quaternized with one mole of DMAEMA and the other mole of DMAEMA in the polymer network but unquaternized.

If the mole ratio of VBC to DMAEMA is increased beyond one to one the polymer will contain unquaternized pendant $-CH_2 Cl$ groups.

When the VBC mole fraction is increased beyond the 1/1 ratio the unquaternized pendant $-CH_2 Cl$ groups of the polymer formed should be capable of being post quaternized. This post quaternization should be accomplished with an amine or a poly-amine to yield a membrane of high functionality. The resulting higher functionality should have lower resistance and very probably improved selectivity over the standard CDLL series.

(See Fig II)

The first polymer membrane made was one with two moles of VBC to one mole of DMAEMA. Considerable difficulty was experienced in producing membranes of minimal quality. Even with the most rigorous processing and fabrication techniques yields of less than 25% were the rule. Despite these poor yields some preliminary membranes were treated with amines in order to develop an awareness of the parameters involved in the post-quaternization step.

The test data on these membranes is found in Table 4.0-I.

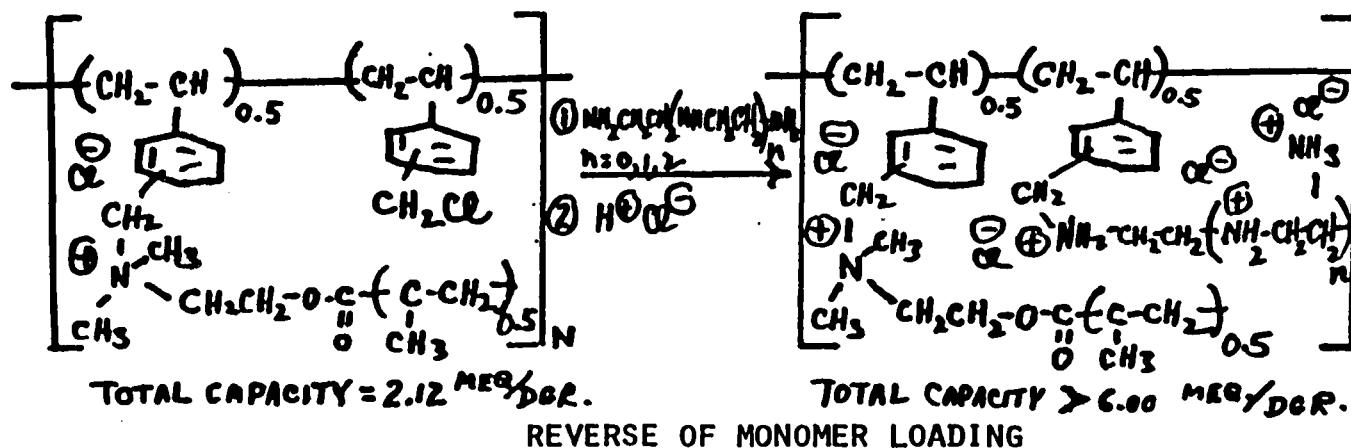
The untreated membrane had a total ion exchange capacity close to the predicted one.

FIGURE II

VARIATIONS IN MEMBRANE SYNTHESIS DESIGNED TO MEET UTILITY LOAD LEVELING REQUIREMENTS

CAPACITY UPGRADING:

INCREASE AMINE FUNCTIONALITY WHILE MAINTAINING 0.5 FORMAL CROSSLINK



BENEFIT EXPECTED:

- A) IF n OF POLYAMINE IS 1 OR 2, EXPECT LARGE REDUCTION IN RESISTIVITY.
- B) IF n OF POLYAMINE IS 1 OR 2, EXPECT LARGE REDUCTION IN FERRIC ION PERM.

TABLE 4.0-I

Post Quarternization StudyPolymer: 2 Moles VCB/₁ Mole DMAEMA

<u>W233-28</u>	<u>No Treatment</u>	<u>Trimethylamine 25% in Methanol</u>		<u>Diethylenetriamine</u>		<u>Tetraethylene- pentamine</u>	
		<u>3 Day</u>	<u>10 Day</u>	<u>3 Day</u>	<u>10 Day @ 45C</u>	<u>3 Day</u>	<u>10 Day @ 45C</u>
NP	.275	.275	.275	.275	.275	.275	.275
Resistance 0.1N HCl (Ω -cm ²)	21.5	7.8	13.8	10.9	Destroyed Backing	12.6	9.8
Thickness (cm)	0.038	-	0.034	-		-	0.036
I.E.C. (meq/d.g.)							
Total	2.13	3.31	2.77	3.42		2.73	3.05
Strong	1.75	3.24	2.39	1.89		1.83	1.74
Weak	0.38	0.07	.038	1.53		0.90	1.31
Water (%)	22.5%	27.3%	32.0%	24.5%		25.9%	25.0%
<u>Theoretical</u>							
I.E.C.							
Total	2.12	3.85	Same	6.28	Same	7.54	Same
Strong	2.12	3.85		3.55		3.08	
Weak	0.00	0.00		2.73		4.46	

Treatment with the tertiary amine, trimethylamine (25% in methanol) gave a limited increase in total I.E.C. The reaction was completed in less than 3 days and some reversion may have occurred on further treatment. The initial high resistance of this compound $21.5 \Omega\text{-cm}^2$ dropped to less than half, however, it still was considerably above the typical CDLL value of 4-5 Ω . The other two compounds tried for post quaternization were polyamines containing both primary and secondary amine groups. Neither performed well at room temperature so a second set of specimens was treated at 45°C for 10 days.

In the case of diethylenetriamine these membranes totally disintegrated - both resin and fabric decomposing. The other polyamine, tetraethylenepentamine which could have yielded an I.E.C. of 7.54 showed only a disappointing total IEC of 3.05 after 10 days @ 45°C. Again the resistivity measurements were disappointing.

In order to verify these values another set of membranes was fabricated in which the mole ratio of the monomers started at 2-VBC to 1-DMAEMA and worked back to a 1/1 mole ratio. Even thus returning halfway (See Table 4.0-II) to the 1/2 mole ratio of the CDLL did little to improve the product membranes. These ratios also resulted in low yields of usable membranes. In view of these difficulties it was decided to suspend work in this area for the present and evaluate other polymer options.

TABLE 4.0-II
High Vinylbenzylchloride Polymers

Code	32R	37-1.5	37-1
Ratio-moles VBC/DMAEMA	2/1	1.5/1	1/1
NP	.275	.275	.275
Resistance 0.1N HCl (Ω -cm ²)	20.7	7.9	5.7
Thickness (cm)	0.034	.034	.034
I.E.C. (meq/dg)			
Total	2.17	2.73	3.35
Strong	2.14	2.73	3.30
Weak	0.03	0.00	0.05
Water (%)	26.2	35.6	38.8
<u>Theoretical</u>			
I.E.C. (meq/dg)			
Total	2.17	2.60	3.24
Strong	2.17	2.60	3.24
Weak	0.00	0.00	0.00

4.1 Dichloroxylylene Membrane Systems

The fabrication of a membrane from p-dichloroxylylene and dimethylaminoethylacrylate was undertaken in the belief that it should produce a membrane equal or superior to the CDLL series. In addition, such a membrane should be substantially less costly than one employing vinylbenzylchloride.

The compound p-DCX is solid and a serious attempt was made to find a suitable solvent for it. Ideally, a solvent for use in this membrane process would dissolve the DCX, be compatible with the DMAEMA, and also dissolve the adducts and polymers formed during the membrane fabrication. It should also wash out of the final membrane easily and completely. A list of most of the solvents screened for this use is listed in Table 4.1-I.

Original efforts centered on reacting two moles of DMAEMA with one mole of the difunctional DCX. The N.P. solvent was a blend of dimethylformamide and methanol. An adduct of the DCX/DMAEMA mix formed with a mild exotherm (around 40°C) and slowly precipitated out of solution. In order to continue the membrane fabrication process the precipitate was filtered from the solution and dried.

Water solutions of these adducts were made. The solutions were catalyzed with sodium bisulfite and potassium persulfate. This gave fast curing systems, even at room temperature.

TABLE 4.1-I

DICHLOROXYLENE
SOLUBILITY STUDY ROOM TEMP.

<u>DCX</u>	<u>SOLVENT</u>	<u>RATING</u>
5g	20 ml cellosolve	Insoluble
5g	20 ml BEP (ether)	Insoluble
5g	20 ml Cyclohexane	Insoluble
5g	20 ml Isobutanol	Partially Sol.
5g	20 ml t-butyl alcohol	Insoluble
5g	20 ml Carbitol (ucc)	Insoluble
5g	20 ml Diethylbenzene	Insoluble
5g	20 ml cyclohexanone	Soluble
5g	20 ml cyclohexane	Slightly Sol.
5g	20 ml Xylene	Insoluble
5g	20 ml N-butanol	Slightly Sol.
5g	10/10 ml Dimethylform- amid/methanol	Soluble

A number of formulations were tried but even with additional heat curing the membranes produced were characterized by low molecular weight and low cross-link density. The membranes produced tended to spall severely in salt water and acid. Generally they were characterized by poor mechanical properties and high water content.

At this point it was decided to make another attempt to develop a one step procedure with a more or less traditional NP/solvent. Work was started using dilute solutions in tetrahydrofuran, t-butyl alcohol and isopropylalcohol. The DCX reaction with DMAEMA was observed to produce an exotherm to about 40°-42°C under these conditions (1 mole to 2 moles at about 50 NP). As the solution of monomers cooled some of the adduct formed precipitated. It was found that reheating to about 40°C would maintain the solubility of the adduct and allow impregnation of the membrane backing fabric. Such fabrics when cured at 60°C overnight gave good membranes which have been characterized. The results of this preliminary characterization are listed below:

<u>Ion-exchange capacity</u>		
Thickness (cm)	0.043	Total 4.04
R(Ω -cm ²) 0.1 HCl	3.9	Strong 3.79
% water	63%	Weak 0.25

Work was continued on this membrane system to define the various parameters involved in its fabrication, to upgrade its properties and optimize its behavior. A number of additional membranes were made wherein the adduct was kept in solution by heating during the processing.

Modifications of the process have yielded membranes with somewhat lower resistance. While some reduction of water content has been achieved the water content still remains high.

One of the optimized membranes was characterized as follows:

CODE: MT254-28

<u>Thickness</u> <u>(cm)</u>	<u>Resistance</u> <u>0.1N HCl</u> <u>Ω-cm²</u>	<u>Ion-exchange</u> <u>Total</u>	<u>Capacity</u> <u>Strong</u>	<u>Water</u> <u>(%)</u>
0.053	3.2	4.36	3.37	60.4

Yields of leak free membranes are high. Work is needed, however, to substantially lower the water content and tighten up the membrane. This will require modifications to increase the solubility of the monomer system and increase the effective cross-link density of the membrane.

Several DCX/DMAEMA adducts were prepared in alcohol/water solutions. To dissolve most of these materials without heat required considerable dilution. Generally membranes prepared from these solutions (water/alcohol) were white, opaque and relatively flexible.

One step preparation with a water/alcohol mixture yielded some membranes of good appearance. One of the better ones (AS192-25) was characterized as follows:

<u>R = Ω-cm² in 0.1N HCl</u>	<u>T (cm)</u>	<u>Water Content%</u>	<u>IEC</u>	
			<u>Total</u>	<u>Strong</u>
3.7	0.047	49.0	4.13	2.78

This membrane was leak tight in the dye test. However, at least in part, due to its high water content its iron selectivity value (423) was poor. The drop from 60% water to about 50% represents an appreciable improvement over previous membranes of this type. Further reduction in the water content of the membrane is needed to produce a viable membrane in this manner.

In most of the work under this task the DCX used has been para- α,α -dichloroxylylene or a material that was predominantly the para form. In an attempt to get an easy processing formulation the use of the lower melting meta- α,α -dichloroxylylene was tried. This isomer was readily soluble in alcohol and appeared quite reactive toward the DMAEMA.

A tray of 5"x5" membranes was attempted using two moles of DMAEMA to one mole of the meta. The batch was cooled and degassed. The reaction was quite rapid and the cured membrane had a good smooth resinous appearance.

The finished membrane, however, spalled rapidly when put in water.

Another set of membranes was prepared using techniques which minimized the time between the start of mixing and the laying of the tray. These also had a fine appearance after curing but likewise spalled when put into water.

To decrease processing time another small set of membranes were made without degassing the mix. These membranes acquired a large number of pinholes during the cure cycle and were discarded.

The improved solubility of the meta and its higher reactivity are very interesting features of this isomer. The meta material at the present time has limited availability not because of high cost or difficulties in production but because of very low demand for these materials.

4.2 Azo Catalyst Studies

In previous studies a variety of polymerization catalysts have been evaluated for the CD1L and similar type membranes before selecting Vazo 64. In this catalyst study it was decided to explore the use of similar azo type catalysts. The ones selected were Vazo 52 (Dupont) and Luazo 82 (Witco).

These catalysts were selected mainly because their activation temperatures were slightly below (Vazo 52) and slightly above (Luazo 82) the activation temperature of the prime catalyst (Vazo 64). Both V-52 and V-64 are solids. L-82, however, is a readily miscible liquid. The number attached to the trade name of these azo catalysts (52, 64, 82) is used by the manufacturer to indicate the centigrade temperature necessary to activate 50% of a solution of the catalyst in ten hours (half life).

Each of the two new catalysts was evaluated in the standard CD1L formulation at three concentrations, 0.0625%, 0.25% and 0.5%. After screening the curing of the catalysts at 0.5% by making 5" x 5" membranes, sets of the regular 9" x 10" anion membranes were prepared.

All sets of the 9" x 10" membranes had good general appearance and were then fully characterized for resistance in 0.1N HCl, ion exchange capacity, water content, thickness and iron selectivity.

One member of the series was checked for selectivity at two iron concentrations. The results of these tests are set forth in Table 4.2-I.

As can be seen in Table 4.2-I the results fall generally within the range of properties one would expect for the prime candidate membrane CD1L. One exception appears in the somewhat high water content (43.7%) of the 0.0625% L-82 group of membranes. This along with its relatively high selectivity value 131 μg of Fe would lead one to surmise the catalyst concentration bordered on the insufficient.

A selectivity test was run on a 0.5% V52 specimen at two concentration. As generally happens this increase in FeCl_3 and HCl concentration from 1.0M FeCl_3 /0.5N HCl to 1.5M FeCl_3 /1.0N HCl produce an increase in the selectivity of more than double for the 24 hr period (28.9 to 62.2 $\mu\text{g/hr/cm}^2$).

Resin fragments of each of these ion exchange polymers were collected. These fabric free flakes were ground and submitted to evaluation by differential scanning calorimetry. The tests were run in air with a heating rate of 5°C per minute. No radical differences were noted between members of the series and a control from the prime candidate membrane AA5-LC. A presentation of the endotherms and exotherms taken from the DSC scans can be found in Table 4.2-II.

TABLE 4.2-I

CDLL-AA5 Type

Code	Catalyst	Catalyst Study		IEC Strong meq/dg	Water %	Iron Selectivity Test	
		Resistance in 0.1N HCl $\Omega\text{-cm}^2$	IEC TOTAL meq/dg			Thickness cm	IM FeCl ₃ /0.5N HCl $\mu\text{g Fe/hr/cm}^2\text{/M/L}$
W233-86A	0.0625% V-52	4.2	4.40	2.04	34.1	0.039	25.9
W233-86B	0.025% V-52	5.0	4.50	2.17	34.0	0.041	19.5
W233-86C	0.5% V-52	4.1	4.49	2.22	32.5	0.042	28.9
						0.042	62.2*
W233-88LA	0.0625% L-82	3.4	4.17	2.34	43.7	0.045	131
W233-88LB	0.25% L-82	4.4	3.86	2.31	32.3	0.043	24.0
W233-88LC	0.5% L-82	4.6	4.19	2.15	33.8	0.045	28.1

*Iron Selectivity test solution 1.5M FeCl₃ with 1N HCl on one side and 1N HCl on other.

TABLE 4.2-II

DIFFERENTIAL SCANNING CALORIMETRY

TRANSITION TEMPERATURES

<u>CODE</u>	<u>CAT.</u>	<u>INITIAL (ENDOTHERM)</u>	<u>(EXOTHERMS) BELOW 351°C</u>	<u>(EXOTHERMS) ABOVE 351°C</u>
86 A	0.0625% V-52	75°C M*	250°C W* 345°C S	407°C S*
86 B	0.25% V-52	80°C M	200°C VW 250°C W 350°C S	415°C S
86 C	0.5% V-52	82°C M	250°C W 325°C S	390°C S 405°C S 415°C S
-LA	0.0625% L-82	81°C M	195°C VW 260°C W 329°C S	390°C S 413°C S
-LB	0.025% L-82	79°C M	250°C W 350°C S	405°C S 410°C S
-LC	0.5% L-82	85°C M	250°C W 340°C S	415°C S
AA5 -Low Cat	.0625% V-64	75°C M	195°C VW 250°C W 345°C S	408°C -S

* V.W. = VERY WEAK W = WEAK M = MODERATE S = STRONG

The results of these evaluations indicate that if it ever becomes necessary either of these two catalysts could be adopted to the production of good quality CD1L type membrane. The performance of the V-52 2, 2'-azobis (2, 4 dimethyl valeronitrile) is very similar to the V64 however it undoubtedly can achieve a full cure at a substantially lower temperature.

This ability to cure the system at 10⁰-20⁰C less will permit the evaluation of several thin interesting fabrics which were previously excluded from consideration because of their tendency to shrink during the cure cycle.

4.3 Evaluation of New Non-Polymer Materials

Evaluation of new non-polymerizable materials was continued. The influence of both the type and amount of NP have been well established. Because of previous work and processing limitations, the NP contents were maintained in the 20-30% range in these membrane systems. As in earlier studies, the lower NP membranes tended to have higher resistances and better selectivities.

The compounds were selected for trial in the standard CD1L type formulation. One of these materials BMEE (Bis 2, methoxyethyl ether) was abandoned as its membranes spalled badly.

The other two liquids n-butanol and 2-ethoxyethanol (cellosolve) selected for evaluation as NP's performed exceptionally well. The membranes produced were of good overall quality, and yields of pinhole free membranes, were, unlike those of most earlier alcohols and ethers tried, excellent.

These tight, rigid membranes were produced in NP ratios of 0.25 to 0.30. The 0.25 NP in the n-butanol series tended to spall somewhat and was dropped from further consideration. The results of the characterization of the 0.275 and 0.30 are included along with those of the cellosolve variations in Table 4.3-I.

The values generally fall in the ranges accepted for the standard NP; isobutanol. The iron selectivity values are good in the lower end of the non-polymerizable range. From these values it was concluded that both of these materials

could be considered as an alternate solvent to the isobutanol used in the prime candidate formulation. At this point, however, the n-butanol was selected for further study largely on the basis of its closer chemical similarity to the prime NP.

TABLE 4.3-1
CD11-LC TYPES

NON-POLYMER VARIATIONS

Code	Construction	Membrane Thickness cm	Resistance in 0.1N HCl $\Omega\text{-cm}^2$	IEC Total meg/dg	IEC Strong meg/dg	Water %	Iron Selectivity $\mu\text{gm Fe/hr/cm}^2\text{/M/L}$	
							(1st 24 hrs)	(2nd 24 hrs)
W233-57	Calendered Modacrylic .275 NP n-butanol	0.042	4.8	3.80	2.10	33.4	18.2	
W223-58	Calendered Modacrylic .30 NP N-butanol	0.036	4.4	3.86	2.03	36.8	25.6	
W233-76	Calendered Modacrylic .25 NP Cellosolve	0.039	5.3	4.37	2.15	32.5	18.8	
W233-68	Calendered Modacrylic .275 NP Cellosolve	0.044	3.9	4.10	2.13	35.5	38.9	41.6
W233-74	Calendered Modacrylic .30 NP Cellosolve	0.038	4.6	4.25	2.09	37.6	53.7	

One further point of interest in Table 4.3-I in the results of the 2nd 24 hours run on the selectivity of one of the 0.275 NP membranes. Here, as was the case in several other selectivity studies, the second twenty-four hour period values were not substantially different from those of the first twenty-four hour period. This indicated that a steady state condition is achieved with reasonable rapidity and at least maintained for some limited period of time thereafter. Several other runs of up to about seven days showed no substantial change in selectivity rate.

4.4 Helium Purging of Monomers

The prime candidate anion resin monomer blend builds polymer through two routes. One of these is the quaternization reaction between the pendant chlorine of the VBC with the tertiary amine group of the DMAEMA. The formation of these ionene linkages is the primary crosslinking mechanism for the chains produced by the polymerization of the vinyl groups on the VBC and DMAEMA.

Much of the earlier work on the prime candidate system has shown this quaternization reaction to proceed easily and early in the membrane making process causing high viscosity mixes etc. Indeed, only through retarding the formation of this adduct by rigorous cooling of the mix during processing have good yields of pinhole free CDLL membranes been achieved. With these factors in mind, increasing the rate of the vinyl polymerization during the early stages of the polymerization cycle is considered as a desirable objective. One way of achieving such an increase is to free this monomer mix of oxygen which retards the onset of vinyl polymerization.

It is generally accepted that when vinyl monomers are storage stabilized with dihydroxybenzenes such as hydroquinone or t-butylcatechol, as are some of the monomers in this mix, any dissolved oxygen present retards the polymerization. This retarding is believed to occur when the oxygen present converts the dihydroxybenzenes to quinones which are true inhibitors of the vinyl polymerization.

It was therefore reasoned that any retarding effects of these polymerization inhibitors could be overcome by purging the monomer system of oxygen with helium and vacuum. This was done immediately before degassing to minimize the readsorption of oxygen by the mix. The two formulations selected for this treatment were the prime candidate (27.5NP and 0.062%V-64) and a similar one with 0.25% V-52 as catalyst which had shown up well in the iron permeability tests.

The membranes were prepared in the usual manner except, just before degassing, helium was bubbled vigorously into the monomer mix while stirring rapidly. After about 15 minutes of helium treatment the gas flow was reduced and a vacuum drawn over the mix. The mix was then degassed for 15 additional minutes and the membranes prepared.

Both mixes yielded good membranes without leaks or defects. These membranes were fully characterized. The results of these tests and the iron permeability studies are delineated in Table 4.4-I. While both these helium flushed membranes gave good permeability values, the selectivity of the V52 catalyzed version, Code 92B (0.25%-V52), was superior.

As these values approached the best results to date an optimization was attempted using the best of the non-prime catalysts, non-prime NP and vacuum degassing. This study is covered in the next section.

TABLE 4.4-I

CDIL-AA5 Type

HELIUM STUDY

<u>Code</u>	<u>Catalyst</u>	Resistance in 0.1N HCl $\Omega\text{-cm}^2$	IEC TOTAL meq/dg	IEC Strong meq/dg	Water %	Iron Selectivity Test	
						Thickness cm	1M FeCl ₃ /0.5N HCl $\mu\text{g Fe/hr/cm}^2\text{/M/L}$
-92 A	Helium flushed	5.8	3.53	1.90	31.0%	0.047	20.2
	0.0625% V-64					0.047	41.9*
-92 B	Helium flushed	4.9	4.31	2.16	32.7%	0.44	14.9
	0.25% V-52					.043	36.1*

* Iron Selectivity test solution 1.5M FeCl₃ with 1N HCl on one side and 1N HCl on other.

4.5 Optimized Catalyst/NP/Purging Study

To further verify the character and properties of the new non-prime catalyst and new non-prime NP solvent two sets of membranes were made up combining the optimum concentration (0.25%) of the preferred new catalyst (V-52) with the most promising new N.P., n-butanol.

One set of these membranes was prepared from monomer mix that was purged with helium immediately before degassing. The other set of membranes was made from an identical batch of mix but was not helium purged before degassing. Both sets of membranes were processed and cured in the usual manner.

The two sets of membranes appeared to be normal. They were characterized for ion exchange values and tested for iron selectivity. The results of these tests can be found in Table 4.5-I. As will be noted the differences between the two sets of membranes are insignificant. The iron selectivity in both cases is very good. On the basis of this test it appears there is no value to helium purging of trace oxygen in this case.

This formulation should be considered for use as a back-up in certain areas. Its characteristic of curing at lower temperatures should prove particularly valuable in conjunction with use of thin fabrics with low softening temperatures, i.e., polyethylene or polypropylene fabrics.

TABLE 4.5-I
CDLL-AA5 Type Optimization
Selectivity Study

Code	Processing	Resistance in 0.1N HCl $\Omega\text{-cm}^2$	IEC Total meq/dg	IEC Strong meq/dg	Water %	Iron Selectivity Test Thickness cm	IM FeCl ₃ /0.5N HCl $\mu\text{g Fe/hr/cm}^2/\text{hr}$
AS193 - 34	Helium Purged	4.9	3.98	2.10	31.2	.042	12.3
	27.5 n-butanol 0.25 V-52						28.8*
AS193 -36	No Purge	4.7	3.96	2.03	31.8	.042	11.8
	27.5% n-butanol 0.25 V-52						28.6* ⁻⁴³⁻

* Iron Selectivity test solution 1.5M FeCl₃ with 1N HCl on one side and 1N NaCl on the other.

5.0 Lower Resistance Fabrics

The evaluation of fabrics for membranes has been a continuing process. At all times on the redox project the use of new, improved or modified fabrics has been explored. The current prime candidate membrane utilizes a thinner modification of the fabric used in earlier systems. In addition to decreasing the size of the stack unit it has contributed a real decrease in the resistivity of the membrane system.

Under this contract an intensified effort was made to find a new fabric backing for the resin component. Both non-woven and woven fabrics were evaluated. Manufacturers contacted included both fiber manufacturers and fiber processors. Primary consideration was given to fibers of polypropylene, polyethylene and modacrylic polymers. Fabrics from multifilament yarns were emphasized over monofilament yarns.

The performance of a membrane does not depend on thickness entirely. Several other factors are of equal or greater importance.

- A. Fabric weight - There is a trade-off between less fabric for lower resistivity and more fabric for structural strength.
- B. Porosity - The softest, most open fabric generally gives the lowest resistance. This is due to thorough saturation with the monomer.

- C. Calendering - Calendering on only one side of a non-woven fabric appears to produce a material with marginal strength and penetration. Heavily calendered or hard fabrics do not appear to saturate adequately.
- D. Monofilaments - The adhesion of the cured ion exchange resin to monofilaments has been marginal in most cases. Apparently the mechanical locking of the resins to the fiber is missing and the bond deteriorates rapidly on ageing.
- E. Uniformity - The mechanical properties of the web of fabric need not be entirely homogeneous, however, coarse fibers or rapid local changes in fabric density should be avoided. These non-uniformities concentrate the mechanical stresses along the areas of rapid modulus change causing cracks and leaks.
- F. Chemical - The fibers must have the desired resistance to the solvent action of the monomers and to the rigors of the strongly acid environment of the Redox cell.

To screen and evaluate candidate fabrics they were impregnated with the standard CDLL-AA5 Low Cat formulation and checked for leaks and electrical resistance. Control membranes, on the standard modacrylic woven fabric, run at the same time, were examined and characterized as necessary.

From the results of preliminary screening, reasonable candidates for further consideration and/or evaluation were selected.

Consultations with potential suppliers were frequent and improved fabrics were submitted by several of them.

Five special woven polypropylenes were evaluated. These were of a very loose and open construction and were considered to be "scrims". These scrims were made up in 5" x 5" size using the CD1L-AA5-LC formulation.

The resultant membranes were checked for properties and their resistance found to be slightly lower than the modacrylic control. Larger (9"x 10") membranes of two of the most promising, with a 20 x 16 and a 14 x 14 thread count were made up in the prime formulation.

After characterization they were shipped to NASA for further evaluation by the Redox Group. The characterization of these membranes is found in Table 5.0-I.

The suppliers have stated these are the thinnest fabrics they have woven in this multifilament configuration. One supplier believed he could use a slightly thinner thread in one direction but the thickness of the other would have to remain the same. Such a change was not expected to have a significant effect on the finished membrane and therefore trials with this fabric were not pursued. These suppliers are aware of our interest and requirements; we remain in contact with them on a continuous basis.

The range of non-woven fabrics available is very extensive. While most of these non-wovens use monofilaments, many of these filaments are of very small diameter.

TABLE 5.0-I

Exploratory Tests
Woven Fabrics - Polypropylene - CD1L-AA5 LC - Multifilament Warp and Spun Filling

<u>Code</u>	<u>Construction</u>	<u>Fiber Thick (mm)</u>	<u>Membrane Thick (mm)</u>	<u>Resistivity 0.1N HCl Ω-cm²</u>	<u>Dye Test</u>
A	(5" x 5") 20/16 scrim	0.50	0.66	4.7	good
B	(5" x 5") 10/18 scrim	0.45	0.66	4.6	good
C	(5" x 5") 20/20 scrim	0.50	0.62	4.8	good
D	(5" x 5") 17/17 scrim	0.50	0.67	4.7	good
E	(5" x 5") 14/14 scrim	0.45	0.57	3.9	good
<u>SCALE-UP</u>					
A	(9" x 10") 20/16 scrim	-	0.62	4.6	good
E	(9" x 10") 14/14 scrim	-	0.57	3.9	good

The number of multifilament non-wovens available is limited. Currently available polymers utilized are many, however, by far the three most common are polyesters, polypropylenes and polyethylenes. The polymer fibers are bonded into sheets in a number of ways. Some of the more common are:

- a) Hot calendering - Smooth hot roll contacts one or both sides of chopped fiber web lightly.
- b) Raised dot calendering - Small circles or squares on surface of a calender roll contact one or both sides of the chopped fiber web to "tack" the sheet together.
- c) Resin Binder - Small amounts of a low solids resin binder are mixed or coated on the fibers. The fibers are then dried or cured.
- d) Felted - Needles pierce the fiber web perpendicularly driving some fibers through and locking the web together.

A number of general conclusions were developed from this work. These were based mainly on mechanical or physical properties.

- a) Random non-woven fabrics had much better resistance to mechanical stresses than the oriented. Cracks tend to develop along fibers in the oriented versions due to anisotropic modules.
- b) Calendered areas where heat or pressure has bonded the filaments together tend to spall off resin.

This often results in an immediate or subsequent leak.

- c) Multifilament fabrics wet out somewhat more readily, however, they are generally less uniform in fiber distribution.

Typical preliminary data for a set of polypropylene, randomly oriented fiber webs can be found in Table 5.0-II. Very thin fabrics are available, these thin fabrics give low resistivities and poor leak test results. The only exceptions appear to be in a melt blown unbonded multifilament polypropylene.

The membranes made from the melt blown fibers in the half and one ounce per square yard varieties were good but somewhat fragile. Occasional coarse fibers produced uneven loads and tended to create handling and processing cracks.

Removal of the cured membranes from the trays was difficult because of their low thickness. At this time, a technique was developed to make leak free, thin membranes from a variety of polypropylene fabrics. Also laminates of two or more fabrics were created.

TABLE 5.0-II

Exploratory Tests
Non-Woven Fabrics - Polypropylene Random Fiber Orientation - CD1L-AA5 LC

<u>Code</u>	<u>Construction</u>	<u>Wgt. Per Sq. Yard</u>	<u>(mm) Thick</u>	<u>Resistivity 0.1N HCl</u>	<u>Dye Test</u>
AC 939	Dot-heat bonded	28.4 g	0.30	2.9	Poor
AC 940	Dot-heat bonded	35.4 g	0.40	3.3	Poor
AC 950	Dot-heat bonded	42.5 g	0.43	3.3	Very poor
AE 592	Melt blown-loose	17 g	0.15	2.9	Good
AE 594	Melt blown-loose	28.4 g	0.24	2.6	Good
AE 620	Dot-laminate	42.5 g	0.37	3.3	Poor
AE 660	Dot-laminate	59.5 g	0.52	3.7	Poor
AE 890	Dot-laminate	-	0.32	3.1	Poor
IA 801	Dot-heat bonded	-	0.21	2.2	Very poor
IA 900	Dot-heat bonded	Very low	0.12	1.5	Very poor

* Multifilament - non-bonded

This permits the use of one fabric for strength and one for ease of saturation, etc.

Some of the thinner and less uniform polypropylene oriented and non-oriented fabrics screened earlier yielded membranes with good electrical but marginal physical properties. In an attempt to upgrade the mechanical properties, various fabrics were cut and plied before impregnation. These combinations were cured as one piece and appear to perform as a single unit. Often the resultant laminate appeared to have substantially improved mechanical properties at the price of only a minor increase in resistance.

A series of single and multiple non-woven polypropylene layered membranes were evaluated for selectivity and other properties. These results, along with a calendered modacrylic control, are included in Table 5.0-III. The use of the thinner fabrics in laminates appears to offer some advantages, however, none of the membranes with resistance below $3.0 \Omega\text{-cm}^2$ exhibited good selectivity.

The best selectivity of this series was exhibited by (T254-12.7) a thick single ply of melt blown polypropylene (0.076 cm). While the resistance of this membrane was not dramatically lower than the control it is well below $4.0 \Omega\text{-cm}^2$ and 10-20% below the average CD1L-AA5-LC or calendered modacrylic equal to typical CD1L-AA5-LC.

TABLE 5.0-III
Woven Polypropylene
CDLL-AA5-LC

Code	Construction	Membrane Thickness cm	Resistance in 0.1N HCl $\Omega\text{-cm}^2$	IEC Total meq/dg	IEC Strong meq/dg	Water %	Selectivity $\mu\text{gm Fe/hr/cm}^2\text{/M/L}$	
							(1st 24 hrs)	(2nd 24 hrs)
MT254-19	Woven Modacrylic 22" x 22" Control	0.040	4.3	3.76	2.05	37.6	23.0	
MT254-19	Woven Modacrylic 22" x 22" Control	0.040	4.3	3.76	2.05	37.6	26.5	
MT254-19	Woven Polypropylene 20" x 16"	0.062	4.6	see above*			21.4	23.1**
MT254-19	Woven Polypropylene 14" x 14"	0.057	3.9	see above*			26.8	30.1**
MT254-9	Calendered Woven Polypropylene	0.059	4.3				52.0	

NOTE * = The ion exchange capacities and water contents were measured only on the woven modacrylic membrane sheet used for the first two tests. All the MT254-19 membranes listed however, were prepared simultaneously for the same batch of impregnating resin and may be expected to be identical except for the fabric content.

** = Moderately higher room temperature may explain some of this difference between the 24 and 48 hr readings. In some cases slightly lower values have been noted for the second twenty-four hour period.

Table 5.0-IV
CDIL-AA5-LC
Non-Woven Polypropylene - Ply Study

<u>Code</u>	<u>Construction</u>	<u>Membrane Thickness cm</u>	<u>Resistance in 0.1N HCl Ω-cm²</u>	<u>IEC Total meq/dg</u>	<u>IEC Strong meq/dg</u>	<u>Water %</u>	<u>Selectivity μgm Fe/hr/cm²/M/L</u>
T-254- 24	Calendered Modacrylic Control	0.040	4.6	3.98	1.85	30.5	26.3
T254-9C	Single Ply* 15594	0.022	2.3				149
T254- 12-7	Single Ply 2.7oz MBPP*	0.076	3.7	4.03	1.95	36.4	23.1
T254- 10F	Double Ply* 15592/15594	0.037	2.2				145
T254- 24A	Double Ply 15592/15592*	0.028	3.0				49.7
T254- 24B	Triple Ply** 91900/15592*/ 91900	0.033	3.1				58.0
T254- 24-C	Double Ply 15592/15594*	0.038	3.0				48.8
T254- 24-D	15592*/91900/ 15592*	0.045	3.2				28.4

NOTE * = Melt Blown Polypropylene
** = Rough Surface

The second best selectivity was obtained with the triple ply lamination of a very thin dot bonded fabric between two light (0.6 oz/yd) melt blown polypropylene non-wovens. This combination yielded a reasonably rugged membrane 0.045 cm thick having a resistance of 3.2 ohms-cm². It appeared to be slightly less selective than the standard membrane.

Three other polypropylene laminates had resistances around 3.0 Ω -cm² and gave substantially poorer permeabilities, that is in the 50-60 μ g/cm²/hr/mol/l range.

Two other polypropylene backed membranes, one a single ply of (1.0 oz) melt blown polypropylene (T254-9C) and the other a laminate of two of these non-woven fabrics (0.6 oz and 1.0 oz), had very low resistances (2.2 to 2.3 Ω -cm²) but extremely poor selectivity. As both of these membranes passed leak tests based upon dye one must question the influence of random coarse fibers and adhesion of the polymer to the fibers.

An additional series of membranes were prepared using the prime candidate formulation CD1L-AA5-LC, and melt blown polypropylene non-woven fabrics as the carrier. Membranes within this series were prepared from the same ingredients and cured at the same time. The values of the characterization for resistance, ion exchange capacity, etc. and the selectivity are listed in Table 5.0-V. Generally speaking the thicker the membrane, in the series, the better the selectivity. The thicker membranes tend to increase in resistance and decrease in permeability.

TABLE 5.0-V
CDLL-AA5-LC
Melt Blown Polypropylene

<u>Code</u>	<u>Construction</u>	<u>Resistance in 0.1N HCl $\Omega\text{-cm}^2$</u>	<u>IEC Total meq/dg</u>	<u>IEC Strong meq/dg</u>	<u>Water %</u>	<u>Iron Selectivity Test</u>	
						<u>Thickness cm</u>	<u>$\mu\text{g Fe/cm}^2\text{/hr/M/L}$</u>
W223-77	Calendered Modacrylic	4.6	4.02	2.27	32.2	.040	23.1
W223-77	Non-woven 15594 single ply	2.6				.021	109
W223-77	Non-woven 15594 double ply	4.0				.042	38.7
W223-77	Non-woven 2.6 oz MBPP	4.8				.063	18.5

The thicker membranes tend to increase in resistance and decrease in permeability. The thicker non-woven, in this study, has about the same resistance as the control (calendered modacrylic) and about the same selectivity. However, because of its greater weight of resin, it may be slower to foul.

These values were plotted on log paper. The resulting graph (see Figure III) approaches a straight line for thickness vs. selectivity with this fabric and ion exchange resin combination.

One of the most interesting fabrics found was a polyethylene based fabric. This fabric was normally manufactured with a very small amount of an acrylic binder to give a sheet with about 70% voids.

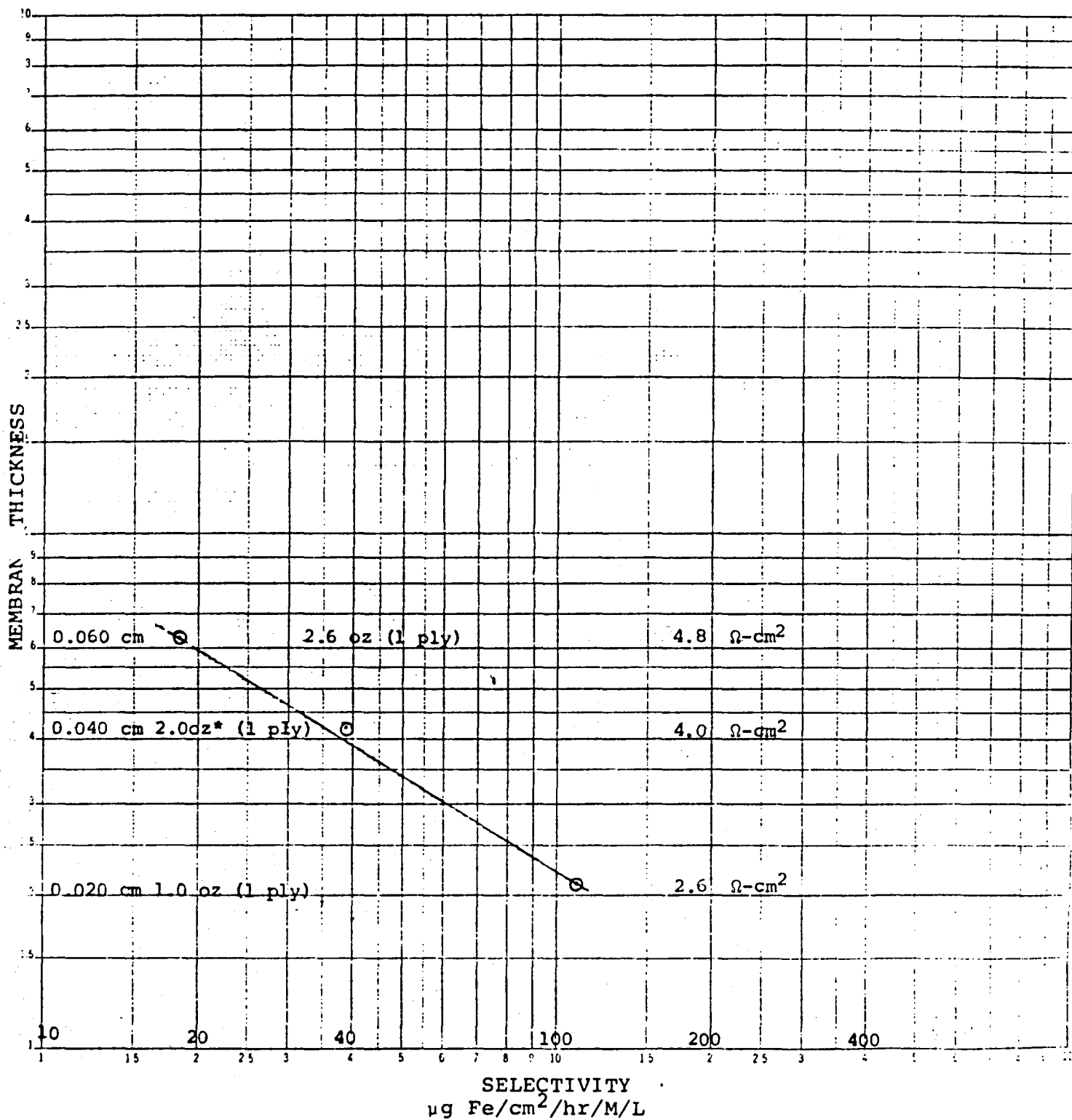
Several varieties of this material were obtained. They were all modifications of this original polyethylene material. Some contained less binder, some no binder and one was another lot of the same material.

Membranes using this random oriented non-woven polyethylene fabric were made mainly with the CD1L-AA5-LC formulation. The results of tests with this fabric are found in Table 5.0-VI. The identification "#-7" is a production lot code of this 0.030 cm material.

The fabric identified "LOW BINDER" was made up by the manufacturer to be more open. It does seem to have produced the best values to date for selectivity with polyethylene.

FIGURE III
SELECTIVITY VS. THICKNESS

CD1L-AA5-LC
On Melt Blown Polypropylene



*Two pieces of the 1 oz fabric cast to make one membrane sheet

Table 5.0-VI
CDLL-AA5-LC
Non-Woven Polyethylene

Code	Construction	Membrane Thickness cm	Resistance in 0.1N HCl $\Omega\text{-cm}^2$	IEC Total meq/dg	IEC Strong meq/dg	Water %	Selectivity $\mu\text{gm Fe/hr/cm}^2\text{/M/L}$	
							(0-24 hrs)	(24-48 hrs)
MT254-19	Typical Calendered Modacrylic	0.040	4.3	3.76	2.05	37.6	23.0	
MT254-24F	Non-Woven Polyethylene #-7	0.030	3.2				56.9	
M223-58 (30 NP n-butanol*)	Non-Woven Polyethylene #-7	0.036	4.4	3.86**	2.01**	36.8**	50.4	
W233-66	Non-Woven Polyethylene Low Binder	0.034	3.6	4.05	2.49	32.2	30.0	28.9

NOTE: * = CDLL-AA5-LC with a modified NP

** = Determined on control membrane (calendered modacrylic)

These sheets show some discontinuties which, presumably, are having some adverse effects on the membrane's performance. Despite its short-comings this sheet is strong, coherent and very intriguing. The use of n-butanol as an NP was included in this series to see if it would wet the backing in a superior manner. Apparently it made little, if any, difference.

The fabricators of this sheet material have stated, that, within limits, it is possible to increase the polarity of the polymer use to make the fibers. Presumably this would increase the wettability of the fabric with our polar monomer systems. It was considered possible that some of the property variations observed during the preparation of the polyethylene and polypropylene based membranes could have been due to poor wetting. Therefore a series of fabrics was treated with a nonionic surfactant to determine if such a treatment would improve the adhesions of the resin mix to the fibers of the fabrics.

The surfactant recommended for the study by one of the non-woven fabric vendors was "Triton X-100". This material was applied to various polypropylene and polyethylene fabrics from 0.1% water solution. The fabrics were dried then overnight at 45°C.

The fabrics treated with "Triton X-100" included a woven polypropylene (21 x 22), a non-woven melt blown polypropylene and several non-woven polyethylenes.

All test fabrics along with a control on the standard untreated modacrylic fabric were converted to AA5-LC type membranes. The control membrane was characterized fully and the other membranes checked for leaks and electrical resistance. All were then evaluated for iron selectivity in the static test cell. The values given in these tests were generally equivalent or slightly poorer than similar ones on fabrics not treated with Triton X-100.

Only in the case of the woven polypropylene fabric did the treatment yield an improved selectivity and even here it was marginal. The results of this test are outlined in Table 5.0-VII.

An observation of particular note was the yellow staining of the membranes by the ferric chloride solution. While no leaks were detected, the yellow staining by the FeCl_3 extended across almost the full diameter of the 2" circular test pieces. Only in the regular modacrylic fabric was the staining restricted to the approximate area of the 3/4" circle of solution contact.

In all the other cases, apparently the solution wicks along the fibers, suggesting encapsulation rather than true bonding by the ion exchange resin. Such wicking probably decreases the selectivity of the membrane.

This study, with its emphasis on non-woven fabrics, developed and extended our ability to make thin leak free membranes.

Table 5.0-VII
CDIL-AA5-LC Type
Wetting Study

Code	Construction	Resistance in 0.1N HCl $\Omega\text{-cm}^2$	IEC Total meq/dg	IEC Strong meq/dg	Water %	Iron Selectivity Test	
						Thickness cm	$\mu\text{g Fe/hr/cm}^2\text{/M/L}$
No Surfac- tant	Cal 386	4.7	4.46	2.26	35.0	0.043	27.3
Same	Same	4.7				0.041	47.2*
No Surfac- tant	Woven poly propylene	4.1				0.055	30.6
X-100 Treated	Woven poly propylene	4.3				0.058	25.0
X-100 Treated	Non-woven 2-199 PE	3.8				0.034	66.1
X-100 Treated	Unbond Sheet-PE	3.6				0.032	43.7
X-100 Treated	Hand Sheet PE	3.0				0.033	46.5
X-100 Treated	2 Ply 15594 MBPP	3.4				0.045	46.8

* This static test cell had 1.5M FeCl_3 + 1.0N HCl on one side and 1.0N HCl on the other side
All other test cells had the 1.0M FeCl_3 + 0.5N HCl on one side and 0.5N HCl on the
other side of the membrane.

It has also taught us how to make laminated membranes and to appreciate the ability of these random non-woven fabrics to distribute the stresses of curing and drying anion exchange membranes. The behavior of these samples in ferric chloride solution has also highlighted the need for a substantial increase in anion polymer to fiber polymer adhesion. This adhesion will be necessary to achieve significant improvements in the properties and performance of polyethylene and polypropylene based membrane systems.

It has also taught us how to make laminated membranes and to appreciate the ability of these random non-woven fabrics to distribute the stresses of curing and drying anion exchange membranes. The behavior of these samples in ferric chloride solution has also highlighted the need for a substantial increase in anion polymer to fiber polymer adhesion. This adhesion will be necessary to achieve significant improvements in the properties and performance of polyethylene and polypropylene based membrane systems.

6.0 Flow Resistivity Testing at Elevated Temperatures

Normally Ionics has run a test characterization of candidate membranes which includes:

Resistance in 0.1N HCl	(ohm-cm ²)
Thickness	(cm)
Water Content	(wt.%)
Ion Exchange Capacity	
Total	(meq/dgr)
Strong	(meq/dgr)
Selectivity	(μgFe/cm ² /hr)

During the latter part of this contract, at the NASA-Lewis Redox Group's request, work was begun to add a Flow Resistivity Test to the standard characterization at Ionics. This test originated by the NASA-Lewis Redox Group is to be used as a screening test for the tendency of candidate membranes to increase in resistance due to iron fouling.

This test consists of pumping a mixture of 1M FeCl₃ and 1N HCl across both sides of the membrane under test. Flow rates of about 100 ml per minute are being used and temperatures maintained in the 60 to 65°C range. The resistance of this "Flow Resistivity Cell" is followed at 1000 Hz. and rated on an ohms per square centimeter basis.

The test cells and auxiliary equipment were supplied to Ionics by the Redox Group. These assemblies have been slightly modified by Ionics with tubing and fittings to permit more convenient operation in the 60 to 65°C temperature range.

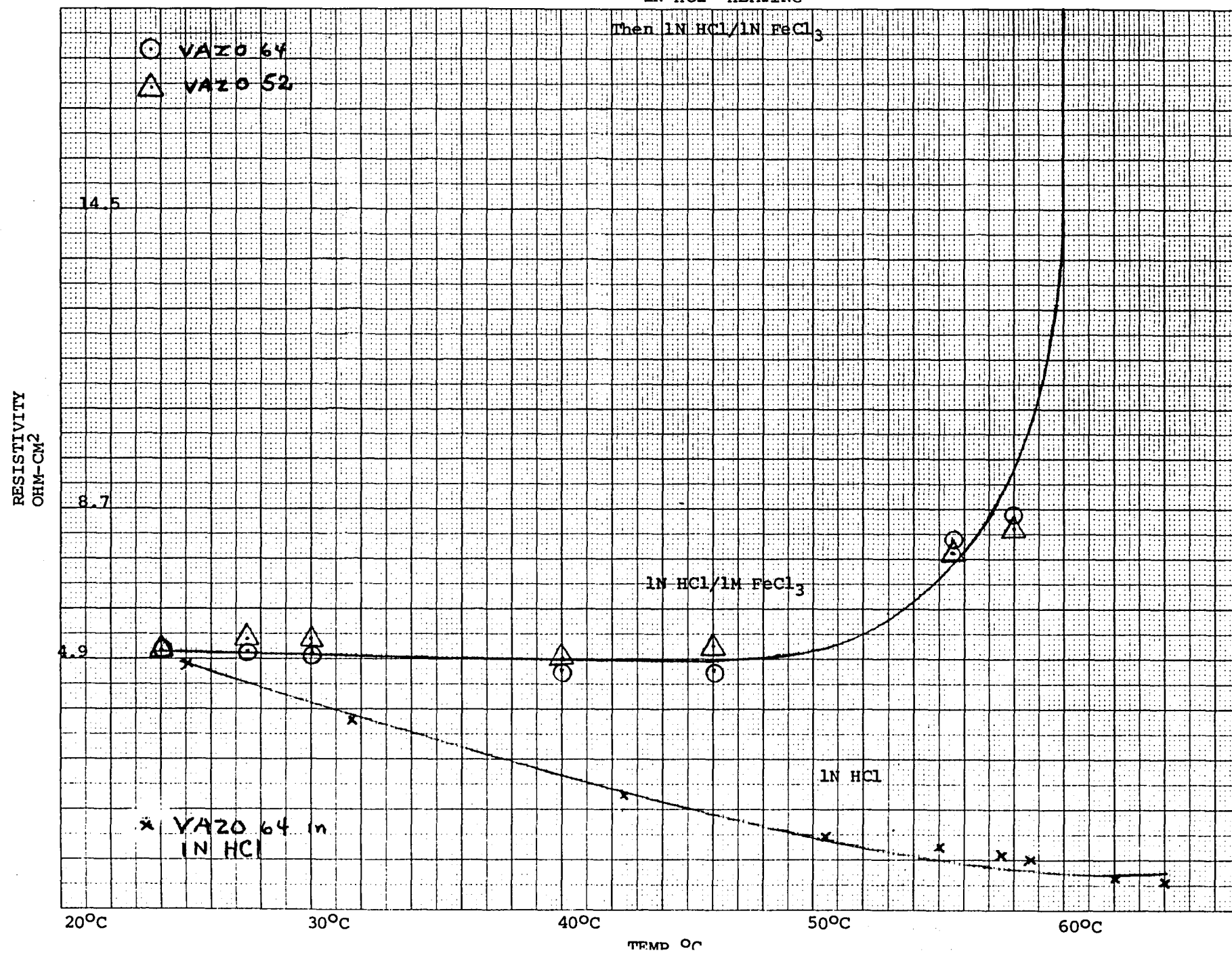
Runs have been made with this unit using the prime candidate CD1L-AA5-LC membrane and some experimental ones. The experimental ones were 20 NP formulations with Vazo 64 and Vazo 52 as catalyst.

To determine base lines the cells were initially operated without membranes with HCl and HCl/FeCl₃ solutions. Subsequently they were operated at 20° to 60°C with membranes in place and various solutions circulating. The solutions of HCl and/or HCl-FeCl₃ used were heated in a bath and then circulated through the cell. Temperature of the thermally shielded cells were monitored by thermocouples. Temperature of the flowing solution also was measured both in the bath and in a reservoir at the membrane cell. Bath temperatures ran about 10° to 15°C higher than cell temperatures.

The behavior of the flow resistivities in HCl and mixes of HCl and FeCl₃ were drastically different. In 1N HCl as the fluid circulating around the membrane increased from 25°C to 60°C the resistance of the cell dropped to about half of its original value. This drop occurred rapidly and even the most minute changes in temperature produced an almost (Fig. IV) instantaneous change in the resistance of the membrane.

When the temperature of the membrane was cooled back to its original temperature, in HCl, they promptly regained their original R values. The curves of temperature vs. R value generated no discernable hysteresis loop on cooling.

Resistivity vs. Temperature
1N HCl HEATING



The behavior of the membranes in a solution of 1N HCl/1MFeCl₃ was much different than in HCl alone. The resistance value of the membrane increased to values ten or more times the original value as the temperature of the solution was raised from 25° to 60°C. It achieved its final or steady state value in about twenty-four hours, (Fig V & VI)

The shape of the curve indicates the HCl component of the solution is probably dropping while the FeCl₃ component is increasing the total resistance.

While membrane of only two NP contents, 20 & 27%, were evaluated it appears, as one would expect, the membrane with the lower NP has the higher resistance and vice versa. It also appears that the lower NP membrane takes longer to achieve equilibrium R value at any given temperature. (Fig VII)

Two catalysts and two catalyst concentrations were evaluated in this series to date. No significant differences in the membranes' performances were noted. Apparently adequately cured membranes perform in a similar manner.

Even the membranes which have shown the greatest increase in R values when cooled and immersed in circulating HCl rapidly drop to their original R value.

This flow resistivity test at 60°C appears to yield fast, reproducible numbers. Its use as a screening test is expected to provide quick, accurate assessment of a membrane's iron fouling tendencies.

Figure V
Resistivity-Temperature-Time
RESISTIVITY
 $\Omega\text{-cm}^2$

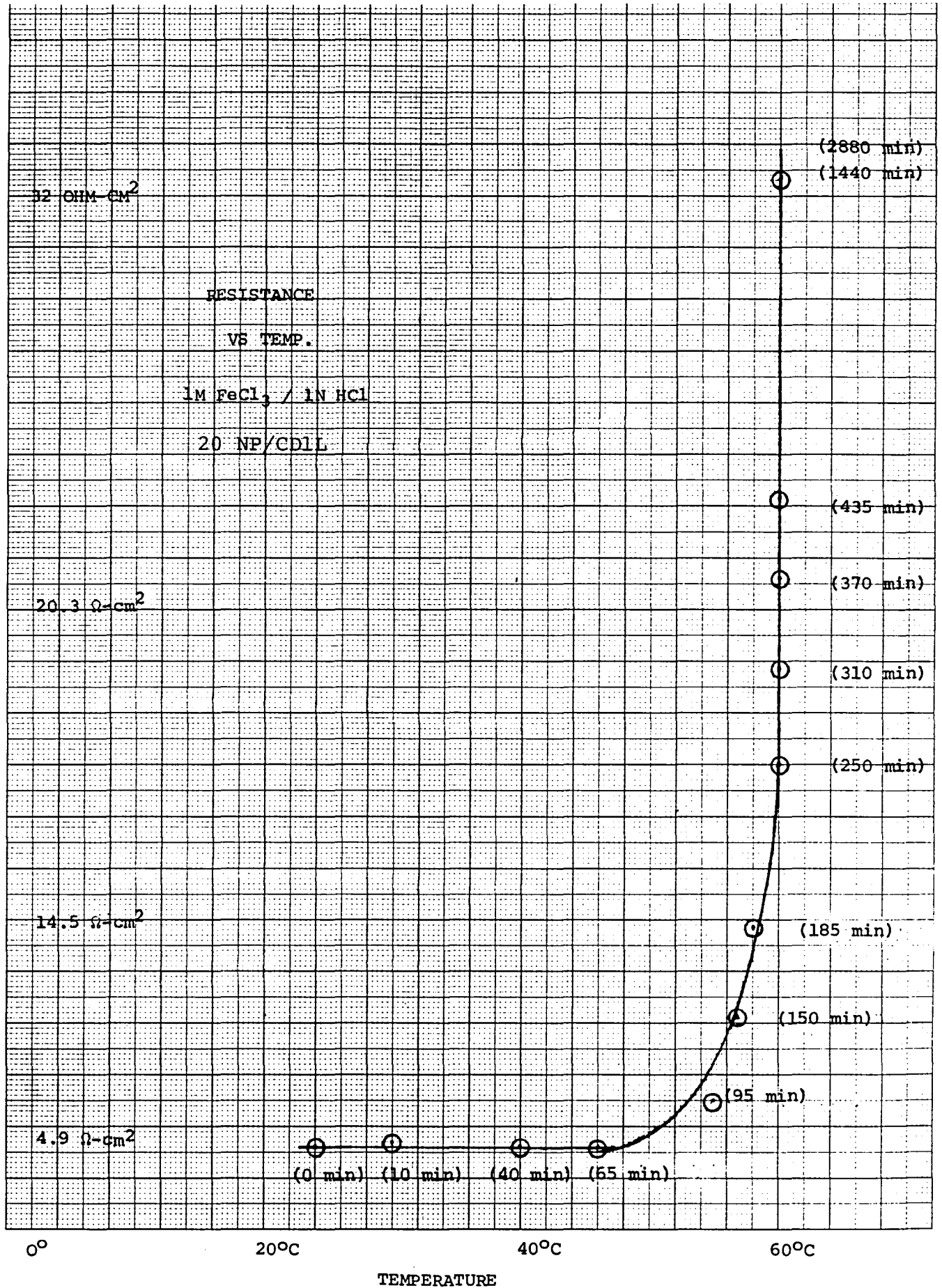


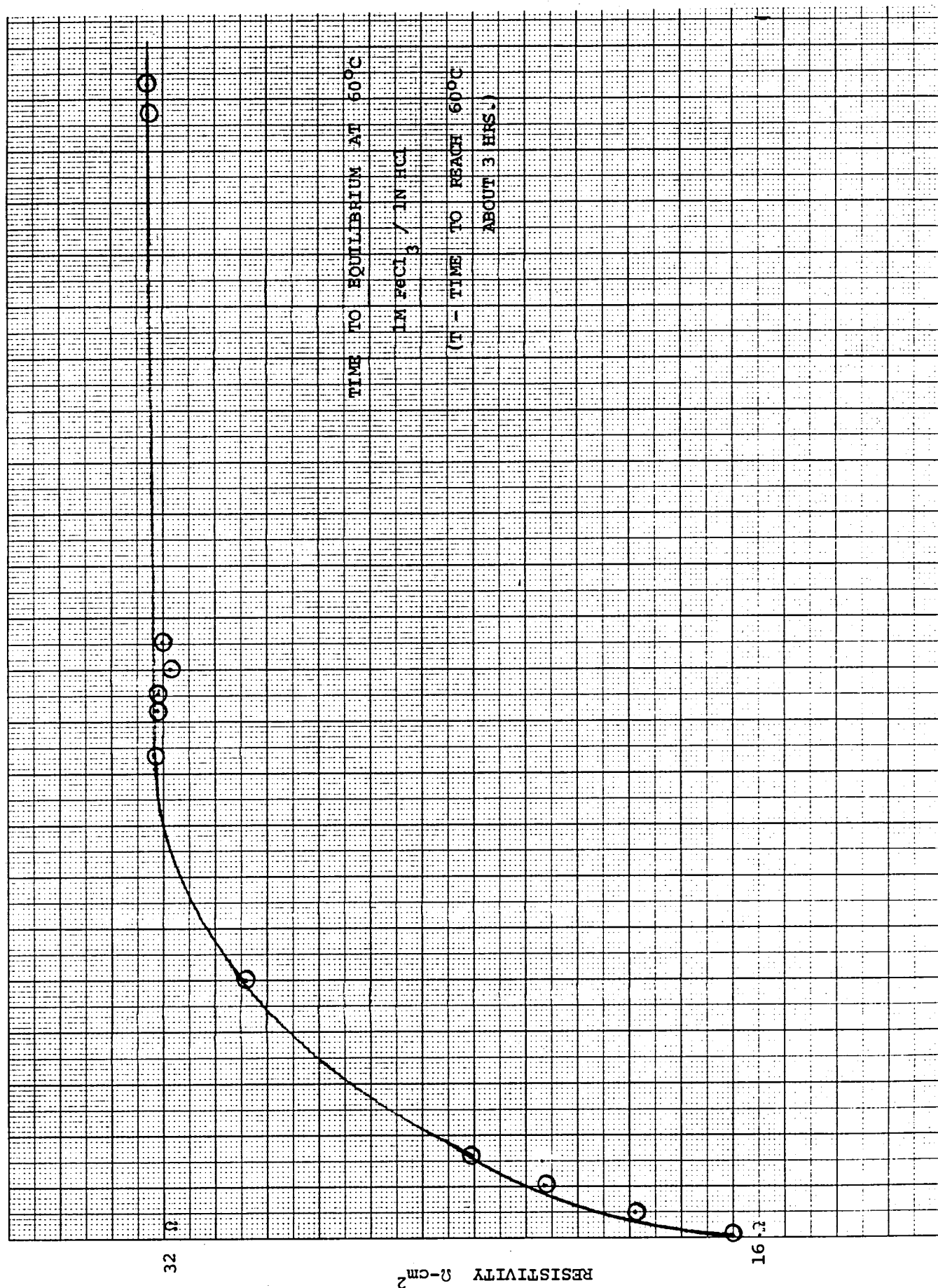
Figure VI 461510

K Σ 10 X 10 TO THE CENTIMETER 18 X 2 $\frac{1}{2}$ CM.
KEUFFEL & ESSER CO. MADE IN U.S.A.

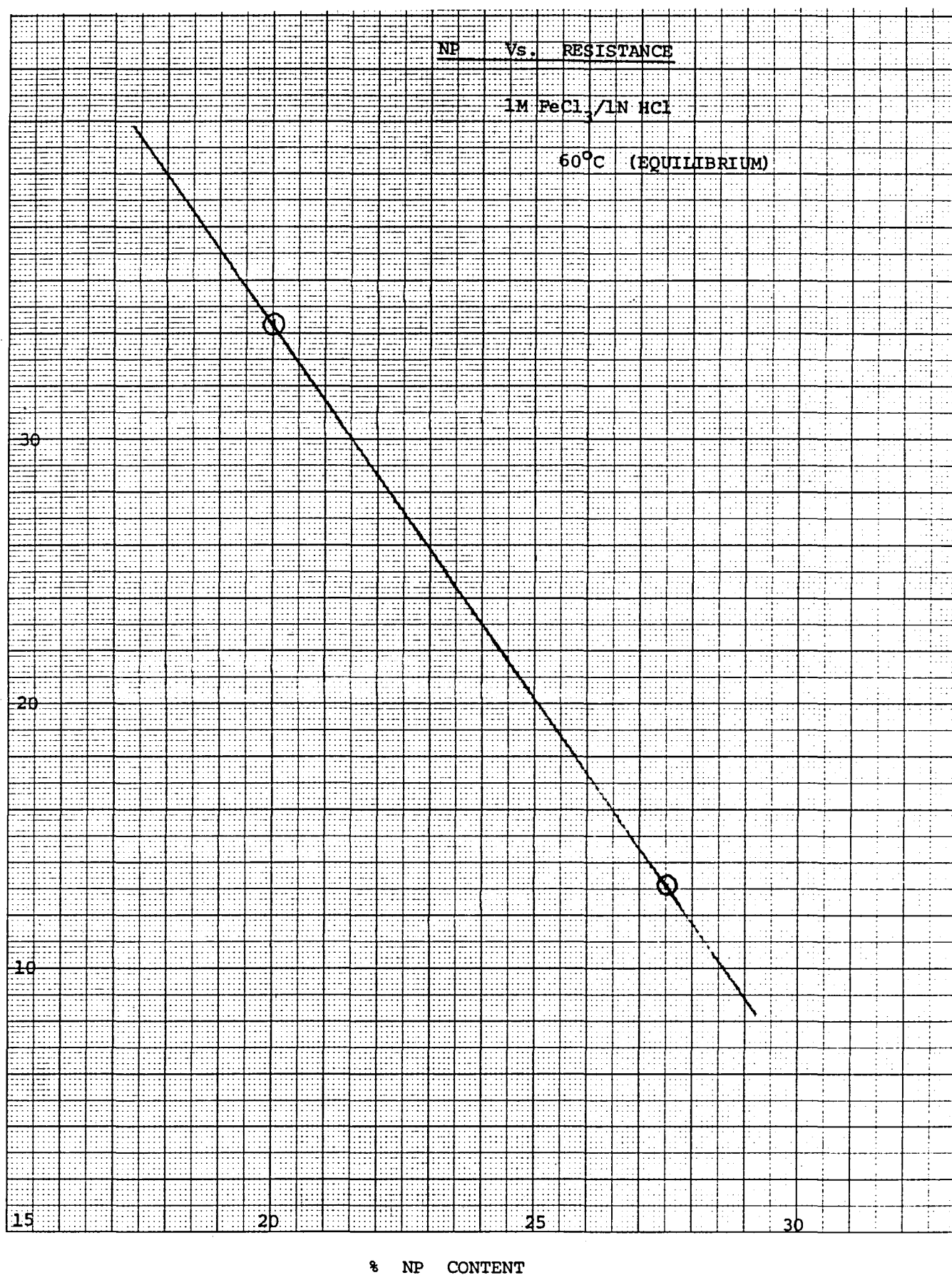
0.25 CATALYST

20 NP

CDLL TYPE



T + 0 HRS T + 10 HRS T + 20 HRS T + 30 HRS T + 40 HRS



461510

K&E 10 X 10 TO THE CENTIMETER 18 X 25 CM
KEUFFEL & ESSER CO. MADE IN U.S.A.

GLOSSARY

IBUOH	- Isobutylalcohol
Cellosolve	- 2 ethoxyethanol
VBC	- Vinylbenzylchloride
DCX	- α, α dichloroxylene
DEB	- Diethylbenzene
DMAEMA	- Dimethylaminoethylmethacrylate
NP	- Non-Polymer Content
CD1L	- #1 Candidate Membrane System - Copolymer of VBC and DMAEMA
IEC	- Ion exchange capacity (meq/dry gram resin)
Permeability	- measured in 1.5M FeCl ₃ with 0.5N HCl - μg of Fe/hr/cm ²

Distribution List

Copies

NASA Lewis Research Center
21000 Brookpark Road
Cleveland, OH 44135

Attn: J. S. Ling, M. S. 30901	10
J. E. Bolander, M.S. 500-312	1
N. T. Musial, M.S. 500-113	1
Library, M.S. 60-3	2
Report Control Office, M.S. 505	1
L. Rosenblum, M.S. 49-5	1
L. H. Thaller, M.S. 301-3	50
A. W. Nice, M.S. 309-1	1
T. T. Serafini, M.S. 49-1	1
J. S. Fordyce, M.S. 309-1	1
W. B. Alston, M.S. 49-1	1
P. Delvigs, M.S. 49-1	1
L. C. Hsu, M.S. 309-1	1
M. Reid, M.S. 309-1	1
R. Gahn, M.S. 309-1	1
Tech. Utilization Office, M.S. 3-19	1
M&S Division Contract File, M.S. 49-1	1
N. Hagedorn, M.S. 309-1	1
S. Hines, M.S. 5-5	64

NASA Scientific & Technical Information Facility
P. O. Box 8757
Baltimore/Washington International Airport, MD 21240
Attn: Accessioning Department

25

NASA Headquarters
Washington, DC 20546

Attn: R. D. Scott, Code RET-1	1
W. H. Johnson, Code RET-1	1
J. J. Gangler, Code RTM-6	1

Sandia National Laboratories
Division 2523
P. O. Box 5800
Albuquerque, N.M. 87185

Attn: R. P. Clark	1
W. Abel	1
R. Glass	1
J. Chamberlin	7

Department of Energy
20 Massachusetts Avenue, S.W.
Washington, DC 20545

Attn: G. F. Pezdirtz, Code 600E	1
A. R. Landgrebe, Code 600E	1
K. W. Klunder, Code 600E	1
M. J. Kate, Code 600E	1
S. Ruby, Code 600E	1

Distribution List

2

Copies

NASA Flight Research Center P. O. Box 273 Edward, CA 93523 Attn: Library	1
NASA Goddard Space Flight Center Greenbelt, MD 20771 Attn: Library	1
NASA Langley Research Center Hampton, VA 23665 Attn: Library N. J. Johns	1
NASA Manned Spacecraft Center Houston, Texas 77001 Attn: Library Code EP	1 1
NASA George C. Marshall Space Flight Center Huntsville, AL 35812 Attn: Library	1
Jet Propulsion Laboratory 4800 Oak Grove Drive Pasadena, CA 91103 Attn: Library	1
NASA Ames Research Center Moffett Field, CA 94035 Attn: Library	1
University of Pittsburgh School of Engineering Chemical & Petroleum Engineering Department Pittsburgh, PA 15261 Attn: Chung-Chiun Liu	1
R.A.I. Research Corporation 225 Marcus Boulevard Hauppauge, L.I., NY 11787	1
ITT Research Institute 10 West 35th Street Chicago, IL 60616	1
Southwest Research Institute P. O. Box Drawer 28510 San Antonio, TX 78228	1
Ionac Chemical Company Division Sybron Corporation P. O. Box 66 Birmingham, NJ 08011	1

Distribution List

3

Copies

Midwest Research Institute
425 Volker Boulevard
Kansas City, MO 64110

1

Stanford Research Institute
Menlo Park, CA

1

HNU Systems, Inc.
30 Ossipee Road
Newton, MA 02164
Attn: J. H. Becker

1

Technical Liaison
Wright-Patterson Air Force Base, OH 45433
Attn: E. E. Bailey, AFAPL/DO

1

1. Report No. NASA (CR#) 167872	2. Government Accession No.	3. Recipient's Catalog No.	
4. Title and Subtitle Anion Permselective Membrane		5. Report Date	
		6. Performing Organization Code	
7. Author(s) Russell B. Hodgdon and Warren A. Waite		8. Performing Organization Report No.	
9. Performing Organization Name and Address Ionics, Incorporated Research Division 65 Grove St. Watertown, Massachusetts 02172		10. Work Unit No.	
		11. Contract or Grant No. DEN 3-204	
		13. Type of Report and Period Covered Contractor Report	
12. Sponsoring Agency Name and Address Department of Energy Office of Advanced Conservation Technologies Division of Energy Storage Systems Washington, D.C. 20545		14. Sponsoring Agency Code DE-AI-04-80-AL-12726	
15. Supplementary Notes Prepared Under Interagency Agreement No. DE-AI-04-80-AL-12726 Project Manager: Jerri S. Ling NASA Lewis Research Center Cleveland, Ohio 44135			
16. Abstract <p>This report covers work on the synthesis and fabrication of polymeric anion permselective membranes for redox systems. Under the synthesis section variations of the prime candidate anion membrane formulation to achieve better resistance and/or lower permeability were explored. Under the fabrication section processing parameters were evaluated to lower cost and fabricate larger sizes.</p> <p>The processing techniques to produce more membranes per batch were successfully integrated with the fabrication of larger membranes. Membranes of about 42" x 20" (107 cm x 51 cm) were made in excellent yield.</p> <p>Several measurements were made on the larger sample 42" x 20" membranes shipped to NASA-Lewis. Among the data developed were water transport and transference numbers for these prime candidate membranes at 20°C. Other work done on this system included characterization of a number of specimens of candidate membranes which had been returned after service lives of up to sixteen months at the NASA Lewis Research Center.</p> <p>The synthesis section includes work with new polymer constituents, the efforts with new N.P.'s, catalysts and backing fabrics. Some work was also done to evaluate other proportions of the ingredients of the prime candidate system. The adoption of a flow selectivity test at elevated temperature was explored.</p>			
17. Key Words (Suggested by Author(s)) Same Last Year		18. Distribution Statement Unclassified - Unlimited Star Category 44 DOE Category UC 94C	
19. Security Classif. (of this report) Unclassified	20. Security Classif. (of this page) Unclassified	21. No. of Pages	22. Price*

* For sale by the National Technical Information Service, Springfield, Virginia 22161

End of Document