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ANION SELECTIVE MEMBRANE

by

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Russell B. Hodgdon

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Watertown, Massachusetts 02172

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Prepared for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

NASA Lewis Research Center
Contract NAS 3-28897

Richard W. Lauver, Project Manager

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16. Abstract

Experimental anion permselective membranes were prepared and tested for their suitability as cell separators in a chemical redox power storage system being developed at NASA-Lewis Research Center. The goals of long-term (1000 hr) oxidative and thermal stability at 80° C in $FeCl_3$ and $CrCl_3$ electrolytes were met by most of the weak base and strong base amino exchange groups considered in the program. Good stability was also shown by several of the membrane substrate resins. These were "styrene" divinylbenzene copolymer and PVC film. At least four membrane systems produced strong flexible films with electrochemical properties (resistivity, cation transfer) suprior to those of the 103QZL, the most promising commercial membrane. The experimental systems also possessed good potential for control and improvement of transport properties and resin stability.

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FOREWORD

This document constitutes the final report for the work accomplished between June 1974 and August 1975 by Ionics, Inc. for the National Aeronautics and Space Administration, Lewis Research Center, under Contract NAS 3-18897 entitled Anion Permselective Membrane.

Dr. Russell B. Hodgdon provided overall program management. The Principal Investigator responsibilities for the program were performed by Samuel S. Alexander with major contributions from R. R. Geoffroy and R. B. Hodgdon.

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

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1.0 INTRODUCTION AND SUMMARY

Energy conservation has become an urgent and major national concern. The realization that most energy sources in common use are finite has spurred efforts to improve efficiencies in energy generation and distribution. To this end NASA is currently engaged in research and development of an electrically rechargeable redox cell system for large scale application in the field of bulk power storage, such as "load leveling" in existing electric generating plants and better utilization of intermittent power sources (solar and windmill-electric).

The NASA redox system consists of a 2-compartment unit, each compartment possessing an inert electrode and a flowing catholyte or anolyte separated by an ion selective membrane. The electrolytes are composed of concentrated aqueous chloride solutions of the redox couple which in this case are Fe^{+2}/Fe^{+3} and Ti^{+3}/Ti^{+4} (or Cr^{+3}/Cr^{+2}) at acid levels of 0.5 to 6.0 N in HCl. On discharge of the cell the following reaction takes place at the electrodes.

$$Fe^{+3} + e \longrightarrow Fe^{+2}$$

$$Ti^{+3} \longrightarrow Ti^{+4} + e \quad (\text{or } Cr^{+2} \longrightarrow Cr^{+3} + e)$$

On the charge cycle the reverse reactions occur.

A critical element in the redox cell system is the ion selective membrane which acts as a barrier to the physical intermixing of the oxidant and reductant ions present in the flowing electrolytes. The membrane also serves as an ion conductive pathway during the discharge and charge cycles permitting the ready transfer of the chloride ion or proton to complete the electric circuit.

The development of the NASA redox system has been limited by the lack of a suitable commercial membrane which could meet the overall requirements in membrane performance of low resistivity (20 ohm-cm or less at 80° C), negligible permeation of reactive ions, and long term oxidative and thermal stability in the given redox environment.

Candidate membranes were prepared which met the resistivity criteria in 1N HCl and also exhibited a 10 to 50 fold decrease in Fe^{+3} permeation over that shown by the 103QZL membrane, the bench mark model used. Polymer structure with at least 1000 to 6000 hrs stability in redox solutions were also identified.

This report represents a year's effort at Ionics, Inc., Watertown, Mass., under Contract No. NAS 3-18897 entitled "Anion Permselective Membrane". Its objective was the development of an improved anion membrane or membranes suitable for long-term application in the redox system. The program was organized and conducted in three major areas:

- selection of at least twelve candidate membrane systems;
- synthesis, testing, and stability evaluation of the candidate membranes;
- identifying the candidate membrane system having greatest potential for optimization of electrochemical properties.

Fifteen membrane systems, each comprising a different resin-ion exchange group combination were investigated and evaluated. Most were selected from the systems described in the submitted technical proposal 74-P-5A (March 1974). Several novel systems were introduced during the course of the program. The desired properties were:

- ion exchange group and resin matrix stability in one oxidant/reductant couple at ambient and 80° C temperatures for at least 1000 hrs of exposure;

- low resistivities in the region of 20 ohm-cm in 1 N HCl;
- low or negligible permeation of reactive cations;
- good potential for control or modification of the electrochemical properties.

High priority was given to tests for long term oxidative and thermal stability in the redox environment at 80° C. The establishment of resin and exchange group stability was considered a logical step preceding long range efforts at optimizing any particular membrane system. This modification resulted in an expansion of the testing program.

The membrane systems represented different methods of membrane fabrication. The majority of membranes involved film formation by bulk polymerization of liquid monomers in solvent by means of heat and free radical initiators followed with activation of the film if needed. Other modes of manufacture were film casting of high molecular weight polymers, and direct activation of preformed film by amination or monomer grafting.

The 103QZL, a standard, commercial membrane manufactured at Ionics, Inc. was utilized as a bench mark model for comparison in performance and properties with the experimental anion membranes developed during the program. The 103QZL is a bulk polymerized membrane consisting of a copolymer of vinylbenzyl chloride (VBC) and divinyl benzene (DVB) (post aminated) possessing trimethyl-benzyl quaternary ammonium ion exchange groups. It is produced in the form of a 20-25 mil strong flexible film containing 4 oz woven dynel fabric backing.

103QZL (System 1) has shown good resin-ion exchange group stability in Fe/Ti redox cell tests at NASA-Lewis, giving steady performance for 6000 hrs at ambient temperature without membrane failure. Our tests at Ionics have also demonstrated good stability for the "styrene" divinylbenzene resin structure of the 103QZL and its quaternary exchange group at 80° C in $FeCl_3$ and $CrCl_3$ solution for at least 1000 hrs, although exchange group fouling occurred.

Substantial improvements in membrane electrochemical properties in terms of lower resistivities and lower transfer of cations (Fe^{+3}) were accomplished and advanced in a number of membrane systems. The membrane systems represented a variety of bulk polymerized resins and activated films, possessing a wide range of strong and weak base ion exchange sites. The weak bases included examples of primary, secondary, and tertiary amines. Weak base amines were proposed as suitable exchange groups for the redox system because in acid medium the amines become strongly ionized and conductive in the form of amine salts. In the category of bulk polymerized resins the candidate systems with favorable electrochemical properties and good potential for improvement were:

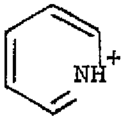
- System 2: a copolymer of 2-vinyl pyridine (2 VP) and ethylene glycol dimethylacrylate (EGDM); membranes A3L-18, A4L-18, and A3L-96.
- System 3: a copolymer of vinylbenzyl chloride (VBC) and EGDM, post aminated with diethylenetriamine (DETA); membranes B2L-DT19 and B2L-DT95.

- System 4: a copolymer of dimethylaminoethyl methacrylate (DMAEMA) and EGDM membranes - CIL-B, CIL-96.
- System 5: a copolymer of DMAEMA and VBC (self-crosslinked linear copolymers) membranes CDIL-56 and CDIL-96.

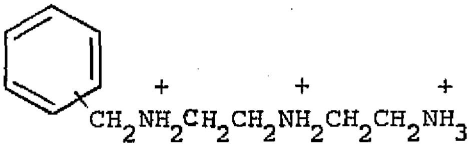
The above membranes were manufactured in the form of 20-25 mil strong and flexible films; virtually free of pinholes and in 1 ft^2 sections.

Substantial reductions in cation transfer were achieved in the above systems as measured by Fe^{+3} permeation. For systems 2, 3, 4 and 5 the Fe permeation factor, P^{+}_{Fe} , fell in the range of 0.03 - 1.4 mg Fe/mF (1.0 mg Fe/mF for the 103QZL).

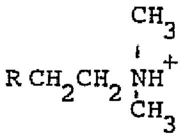
Resistivities measured in 1N HCl by the liquid junction method were 14 to 26 ohm-cm at 80° C and 46 to 96 ohm-cm at ambient temperature. The ion exchange capacity range was 3-5 meq/dgr and represented a spectrum of weak base amino groups and one novel quaternary group.



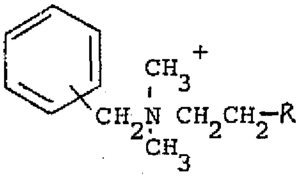
Byridinium HCl,
System 2



Diethylenediamine,
Benzylamine
System 3



Dimethylaminoethyl
System 4



Quaternary amine
System 5

The weak base amino groups were found to be very stable and virtually unaffected in $FeCl_3$ and $CrCl_3$ acid test solutions at 80° C (1000 hr test). The quaternary group of the system 5 membrane (CDIL) which also formed the crosslink segment indicated some deterioration in $CrCl_3$ at elevated temperature.

The substrate polymers for systems 2, 3 and 4 were crosslinked by EGDM, a diester. EGDM was found to be unsuitable for candidate membranes intended for use at elevated temps, as it tended to hydrolyze at 80° C, especially in $CrCl_3$ solution. Resin stability was evaluated by water content analysis (increased H_2O = chain splitting) and physical condition of the resin (erosion, etc.). Deterioration of the resin was severe in system 2, and moderate in systems 3, 4 and 5. However, membranes containing EGDM appear to be feasible for redox use at ambient or moderate temperatures. No visible deterioration was noted in System 2 membranes in 1000 hrs at ambient temperature in $CrCl_3$. EGDM was originally recommended for use in membrane synthesis because of its superior resistance to acid hydrolysis in relation to other monomeric esters (EGDM has no H in the α carbon position); and for its potential in producing resins with high IEC.

The resin stability of systems 2, 3, and 4 can be greatly improved by the replacement of EGDM with high purity DVB (72%) by providing a polymer matrix similar to that of the 103QZL membrane.

Another promising membrane was obtained in candidate system 8 by the amination of polyvinyl chloride (PVC) film with tetraethylenepentamine (TEPA). Post treatment of the membrane by heat (80° C in $FeCl_3$) reduced the porosity and consequently the transfer of cations (Fe^{+3}) by a significant

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amount with a moderate loss in IEC but no change in electrical resistivity. The PVC membrane (VC1-TP8X) is an 8 mil strong and flexible film storable in the dry state and has good potential for further improvement in electrochemical properties. It has shown high current density performance during tests at NASA-Lewis.

A number of other polymer systems were tried with varying results. Three novel resins were prepared by the copolymerization of linear vinyl monomers capable of in situ crosslinking during the bulk polymerization step. Several had exceptionally stable IEC in region of 4-5 meq/dgr but failed to produce leak free useable membranes.

A membrane was synthesized by polymerizing and grafting VBC to low density PE film which had been pre-crosslinked by irradiation. The film was activated by amination with trimethylamine (PV7-8T49, PV8-T49). The porosity of the membrane was unsuitably high.

A membrane system was prepared by the homogenous amination of dissolved PVC followed by solvent casting of the film from the reaction solution (G4-27). The process failed to produce a coherent film.

A scheme to affix amino groups to several different polysulfone resins was unsuccessful. The process involved nitration of the polysulfones followed by reduction to the amines. Nitrogen contents of .7 to 4.3% were obtained in the nitration step but no exchange activity was found in the end products.

A glossary of the candidate membrane systems and an evaluation summary is given in Table 1.

2.0 CANDIDATE MEMBRANE SYSTEMS: SYNTHESIS AND EVALUATION

The candidate membrane systems investigated in this program represented at least four different types of membrane manufacture.

- Thermoset (crosslinked) film formed by bulk polymerization of liquid monomers in a solvent involving heat and free radical initiators. The films contained synthetic fabric backing. The majority of candidate systems were in this category and included the membranes 103QZL, A3L-18, A4L-18, A3L-96, B1L Series, B2L Series, CIL-96, CDIL-96, CP2L-64 and CE-1. Some were made in a one-step process with ionogenic monomers and some required post amination to activate.
- Unbacked preformed thermoplastic commercial (PVC) reacted directly with an amine to create active sites. These were the membrane series VC1-TP1 to VC1-TP8.
- Unbacked preformed thermoplastic film (LDPE) into which styrene type monomer was polymerized and grafted to the base polymer and followed by post-amination to create active sites. These were the membranes PV7-8T49, PV8-T49.
- Unbacked thermoplastic films formed by solvent casting of high molecular weight polymers pretreated to introduce amine groups or precursors to the amino group. These included two types of polysulfone resins and a polyvinyl chloride resin.

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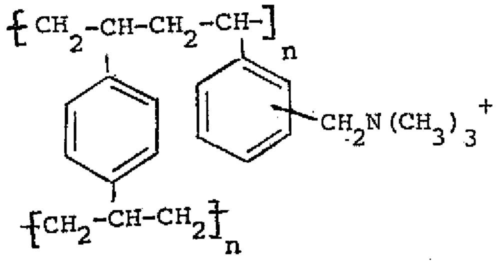
A wide variety of amino exchange groups were utilized in the membrane synthesis program, representing different structures and types of amines and polyamines. These included examples of primary, secondary, tertiary, and quaternary amines mostly in the form of alkylamines or polyalkyl polyamines. One cyclic aromatic amine (pyridine) was used. The chemical and thermal stabilities of these groups and the supporting polymer matrix were studied in the redox environment. (Table 3)

The chemical and physical properties of the candidate membranes prepared in this program are summarized in Table 2.

2.1 The 103QZL-219 Membrane: System 1

The AR103QZL membrane, a standard low porosity membrane manufactured at Ionics, Inc., is a copolymer of vinylbenzyl chloride (VBC) and divinylbenzene (DVB) post reacted with trimethylamine (TMA). The membrane is a strong flexible film 20-25 mil in thickness supported by 4 oz dynel fabric which imparts a burst strength of about 140-160 psi. The film is formed by the bulk polymerization of the monomers in diethylbenzene solvent with the action of heat and benzoyl peroxide initiator. The polymer network consists of a vinyl backbone crosslinked by a benzenoid structure and contains the strong base anion exchange group, benzyl trimethyl ammonium chloride.



Inclusion of this membrane in the testing program served as a bench mark or standard against which the candidate membranes could be compared. It was also used to determine the stability of the benzyl trimethyl ammonium chloride quaternary group.

The supporting polymer structure and the quaternary exchange group showed very good long term stability in the redox test environment at elevated temperature and in actual redox cell operation at ambient temperature. Only negligible changes in IEC or water content were observed after approximately 1000 hrs of exposure to 2 M aqueous solutions of $FeCl_3$ and $CrCl_3$ (both 1 N in HCl) at 80° C. Changes measuring less than ± 5% were considered negligible. The membrane also exhibited no sign of resin erosion, gross defects, or leakage. Some fouling or plugging of the membranes pore structure was indicated however by a substantial decrease in Fe permeation (P^{+}_{Fe}) from 1.0 to 0.38 mg Fe/mF and a rise in contact electrical resistivity (ρ^{c}) from about 160 ohm-cm to 210 ohm-cm after immersion in $FeCl_3$ for 1054 hours (Table 3).

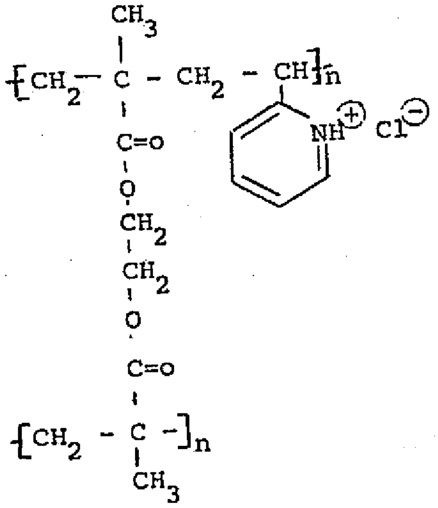
Similar results were obtained for a 103QZL sample on test in a $FeCl_3$-$TiCl_3$ redox cell system at the NASA-Lewis Research Center. The cell functioned continuously for 6000 hours without failure of the membrane which was exposed to both 1 M and 2 M concentrations of the redox couples at 0.5 N and 6N HCl at room temperature (letter of 5/15/75 P. O'Donnell).

Analysis and inspection of the membrane showed no resin erosion, gross defect, or leakage; however, there was some discoloration giving the appearance of a metallic surface sheen. Although there was no evidence of structural deterioration, the analytical data also indicated possible fouling or plugging of the surface pore structure. The IEC loss was 21%, the water content declined by 10%, and the electrical resistivity (ρ^c) increased by 34% in 0.1 M HCl. The Fe permeation showed a substantial decline of from 1.0 to .07 mg Fe/mF, a trend which by itself is favorable to the redox cell process.

The performanance of the 103QZL in redox cell operation represented a middle range among the various candidate membranes on test at NASA-Lewis. The reported output current density was 15 ASF and the cell electical capacity half life was 256 hour.

2.2 A3L-18, A4L-18, and A3L-96 Membranes: System 2

The A3L and A4L candidate membrane group is based on a copolymer of 2-vinyl pyridine (2 VP) and ethylene glycol dimethacrylate (EGDM). The films are formed in one step by the bulk polymerization of the monomers by means of heat and azobisisobutyronitrile initiator. No post treatment is needed to activate or attach the ion exchange group. The membranes are strong flexible films about 20-25 mils in thickness supported by 4 oz dynel fabric. The polymer network consists of a vinyl backbone crosslinked by a methacrylate diester and contains tertiary heterocyclic nitrogen at the exchange site.



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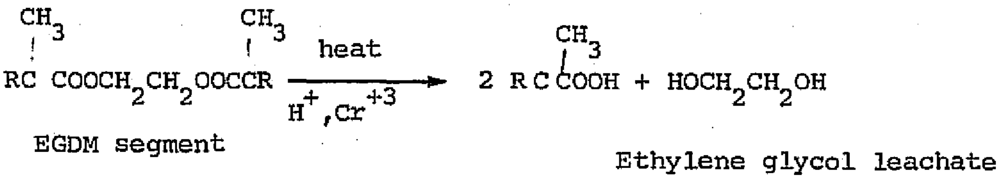
The membranes in this candidate system represent three different polymer formulations with variations in crosslinking, IEC level, and non-polymerizing solvent concentration. A3L-18 and A3L-96 were prepared with the same crosslinking and IEC (3.1 meg/dgr) but the latter with a lower porosity or water content (43.3 and 39.8% respectively). A substantial decrease in Fe transfer was obtained (a change in P^{+}_{Fe} from 1.4 to .066 mg Fe/mF) by only a small decrease of solvent content in the A3L-96 formulation, keeping other factors constant. The A4L-18 was prepared with lower cross-linking and consequently a higher IEC of 4.3 meq/dgr.

A wide variation in polymer stability at elevated temperature was noted for this group (Table 3). The data indicated moderate to substantial hydrolysis of the EGDM cross-linking segment of the resin in $CrCl_3$ test solution which produced swelling, leakage, and erosion in the membranes. The water content progressively increased with time, going from 39.8% to 66.6% for the A3L-96 membrane after 1293 hours of exposure in $CrCl_3$ test solution at 80° C. $FeCl_3$ appears to be a less aggressive solution with regard to EGDM degradation, showing less rise in water content over the same period of time. However, some visible erosion or resin deterioration was noted in all samples.

The increase in apparent IEC was due to hydrolysis and leaching out of the non-ionic component of the polymer structure, ethylene glycol. The hydrolysis or cleavage of an ester produces its constituent carboxylic acid and alcohol.



$$\mathrm{R\overset{CH_3}{C}\,COOCH_2CH_2OOC\overset{CH_3}{C}R} \xrightarrow[\mathrm{H^+,Cr^{+3}}]{\text{heat}} 2\;\mathrm{R\overset{CH_3}{C}COOH} + \mathrm{HOCH_2CH_2OH}$$

The higher electrical conductance in the partially degraded samples was consistent with increased acid diffusion into the swollen polymer matrix. Although EGDM is not sufficiently resistant to chemical attack at 80° C, it appears to be useable in membranes operated at ambient or moderate temperatures. A sample of A3L-86 showed no sign of erosion, swelling or other damage after over 1000 hrs exposure in the acid $CrCl_3$ test solution at room temperature (~ 25° C). No obvious physical damage was observed for membranes A3L-18, A4L-18 and A3L-96 used in redox cell tests conducted at ambient temperature at NASA-Lewis. It was also reported that A3L-18 showed a favorably high output current density at 19 ASF.

Resistance of this polymer system to chemical and thermal attack could be greatly improved by the substitution of 72% DVB for EGDM as the crosslink monomer without serious change in the membrane's electrochemical properties.

Evaluation Summary:

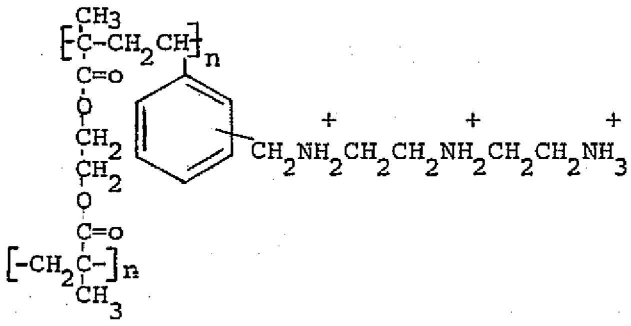
- rugged flexible film
- high stable IEC in region of 3-4 meq/dgr
- low Fe permeability
- ease of manufacture in one step bulk polymerization process - no post-treatment required
- can be manufactured in 3 x 3 ft areas

- useable at elevated temperatures if crosslinked with 72% DVB
- good potential for control of transfer properties by formula modifications
- film thickness reducible for improvement in electrical resistance.

2.3 The B2L-DT 95 Membrane: System 3

The B2L-DT95 (also B2L-DT19) candidate is a copolymer of vinylbenzyl chloride (VBC) and ethylene glycol dimethacrylate (EGDM) post aminated with diethylene triamine (DETA). The monomers are bulk polymerized in the presence of diethylbenzene solvent by heat and benzoyl peroxide initiator. The polymer film, backed by 4 oz dynel fabric to impart strength and flexibility, is aminated in 100% DETA at 50° C to create amino exchange sites. The finished membrane is a rugged film 20-25 mil in thickness possessing a high weak base exchange capacity (5.4 meq/dgr) which comprises secondary and tertiary amine groups.

The polymer structure consists of a vinyl backbone and crosslinkage and contains pendant benzyl amino ethyl amino exchange groups.



The B2L-DT95 candidate had the highest IEC (5.4 meq/dgr) and lowest Fe permeability (P^{+}_{Fe} = 0.029 mg Fe/mF) shown by any membrane

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evaluated in this program. The high selectivity predicted for this membrane was confirmed by redox cell tests at NASA-Lewis which reported that the B2L-DT95 membrane produced the longest estimated half life in cell electical capacity (~400 hrs). However its electrical resistivity in 1 M HCl was higher than that of the 103QZL, a difference consistent with results at NASA-Lewis which reported output current densities of 15 ASF for the 103QZL and 11 ASF for the B2L-DT95.

The direction for immediate improvement of the B2L-DT95 candidate system would be

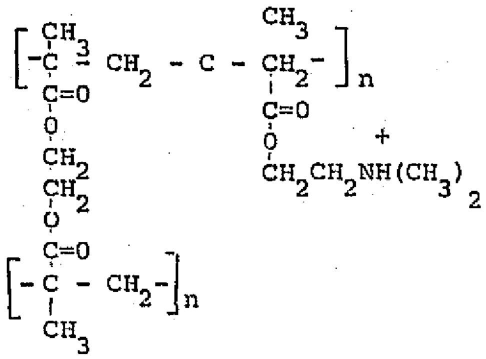
- substitution of 72% DVB for EGDM to insure stability at elevated temps ;
- decrease electrical resistance by increasing IEC and reducing film thickness;
- further reduction in Fe transfer by solvent reduction in formulation.

<u>Evaluation Summary</u>:

- rugged flexible film;
- high stable IEC in region of 5-6 meq/dgr;
- low Fe permeability;
- good potential for control of electrochemical properties by formula modification; could be manufactured in sections up to 3 x 3-1/2 ft ;
- substitution of 72% DVB for EGDM would insure high temp stability;
- film thickness reducible for improvement in electrical resistance.

2.4 The CIL-96 Membrane: System 4

The CIL-96 membrane is a copolymer of dimethylaminoethylmethacrylate (DMAEMA) and EGDM. The membrane is formed in one step by the bulk polymerization of the monomers in the presence of isobutanol solvent by heat and azobisisobutyronitrile initiator. The film is 20-25 mil in thickness and is backed by 4 oz dynel fabric which imparts strength and flexibility. The polymer structure consists of a vinyl backbone with diester crosslinks and contains a pendant tertiary amino group dimethylaminoethyl as the exchange site.



The stability data was similar to that of the B2L-DT95. No change was measured in IEC indicating that the ester linkage connecting the ionized amino group to the vinyl backbone was unaffected by the test environments.

However some hydrolysis of the EGDM was indicated. The water content of the membrane samples increased by 15-20% over a period of 1293 hours exposure time in $FeCl_3$ and $CrCl_3$ test solutions at 80° C. Moderate resin erosion was also observed in $FeCl_3$.

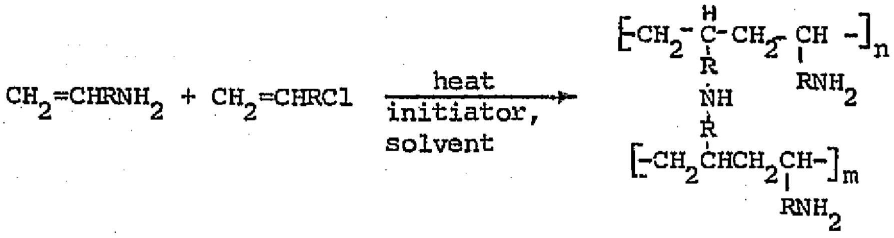
Improvement in polymer stability could be achieved as in the previous candidate systems by substitution of 72% DVB for EGDM. This system also has good potential for control of electrochemical properties by modifying the formulation with respect to solvent, crosslinking and monomer content.

Evaluation Summary:

- rugged flexible film
- stable IEC in region of 3.3 meq/dgr
- low Fe permeability
- good potential for control of electrochemical properties by formula modification
- ease of manufacture in sections up to 3 x 3-1/2 ft
- substitution of 72% DVB for EGDM would insure high temp stability
- film thickness reducible for improvement in electrical resistance
- disadvantage: gave erratic performance in NASA redox cell test.

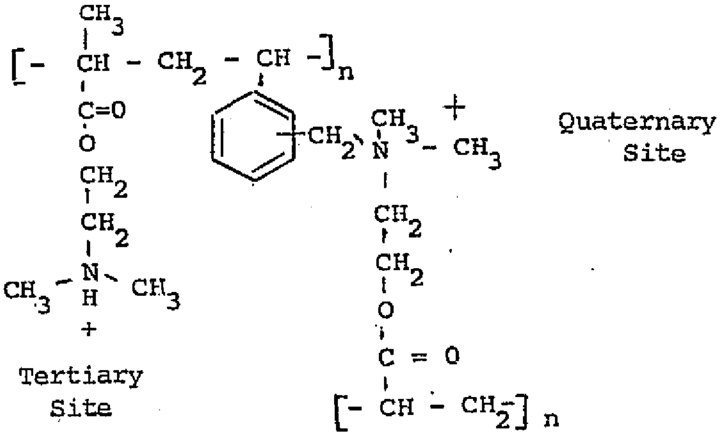
2.5 The CDIL-56 and CDIL-96 Membranes: System 5

The CDIL-series membranes are one of a class of novel self-crosslinked linear copolymers developed at Ionics during the contract period. This resin was obtained by the polymerization of at least two vinyl comonomers each of which normally forms linear polymer chains; but because each contains a reactive site (i.e. an amino or chloro group) an *in situ* condensation reaction occurs which produces crosslinks at the exchange site.



$$CH_2{=}CHRNH_2 + CH_2{=}CHRCl \xrightarrow[\text{initiator, solvent}]{\text{heat}} [-CH_2-\overset{H}{C}(R-NH-R-)-CH_2-CH(RNH_2)-]_n\,[-CH_2CHCH_2CH(RNH_2)-]_m$$

The CDIL membranes are prepared by a bulk polymerization process similar to that used for the A3L and C1L polymer systems. The linear monomers VBC and DMAEMA are polymerized in the presence of isobutanol by heat and azobisisobutyronitrile initiator. The crosslinks are formed by the <u>in situ</u> condensation of the amino group of DMAEMA and benzylchloride of the VBC. The crosslink reaction also produces a quaternary ammonium exchange site. The resin contains both strong and weak base IEC groups, the latter being the tertiary amine of DMAEMA which has not crosslinked.



The total IEC of the CD1L-96 membrane was 4.1 meq/dgr with a 50/50 division in weak and strong base exchange groups. The films were 20-25 mils in thickness and contained 4 oz dynel fabric to give the membrane strength and flexibility.

Stability in the redox test solutions at 80° C was only fair. Resin erosion and 10-20% increase in water content indicated some degradation at the polymer crosslinks. Substantial loss of strong base IEC was measured after 1293 hours immersion time in $CrCl_3$ test solution at 80° C.

Some synthesis difficulty was encountered in reproducing large sections (1 ft^2) free of cracks and pinhole leakage reproducibly. However sufficient areas were made to complete the necessary lab scale tests.

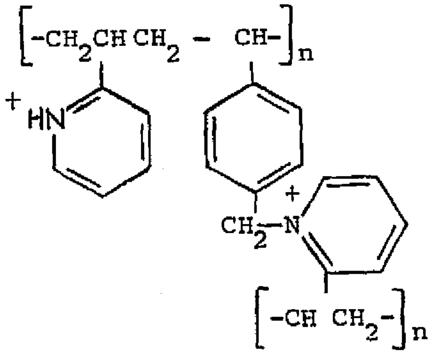
A variant in this system was prepared by converting the tertiary amine groups in a sample of CD1L-56 to quaternary amines by alkylation with dimethyl sulfate. This was accomplished but with some loss in total capacity (CD1L-66Q, Table 2).

Evaluation Summary:

- rugged flexible film
- high capacity containing both strong and weak base IEC
- low Fe permeability
- ease of manufacture by one step process- no post reaction needed
- linear polymers self-crosslinked - no conventional crosslink agent needed
- disadvantages: new chemistry requires further R&D.

2.6 The CP2L-64 Copolymer: System 6

The CP2L ion exchange resin series is another example of an *in situ* self-crosslinked linear copolymer system. The membrane is prepared by a one-step bulk polymerization of vinylbenzyl chloride (VBC) and 2-vinylpyridine (2-VP) in isobutyl alcohol using heat and azobisisobutyronitrile initiator to effect the overall reaction. The resin structure consists of a vinyl backbone crosslinked by the condensation of the pyridine nitrogen and benzyl chloride of the VBC which forms a pyridinium quaternary ammonium site.



A series of formulation and polymerization process variables were explored . These included initiator concentration, monomer crosslinker ratios and solvent content (Tables 4,5). Some improvement in the film and products were obtained but no acceptable whole film suitable for testing of transfer properties was produced. However a sample of the CP2L-64 polymer (equivalent to CP2L-56) was tested for the oxidative and thermal stability of the novel resin matrix and exchange group in the redox environment. (See Table 3).

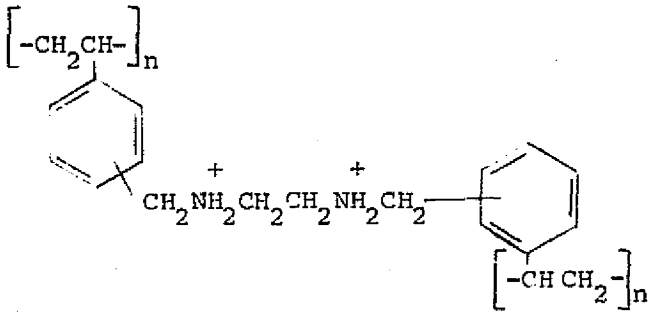
As manufactured the CP2L-64 resin had a total IEC of 4.2 meq/dgr comprised about 60/40 of weak and strong base proportions. About 15% of the strong base IEC was lost after 1054 hours in $FeCl_3$ test solution at 80° C. There were small fluctuations in the resin water content which did not appear to be consistent with the loss of crosslinkage inferred from the decrease in strong base IEC. However, there was severe resin erosion in $FeCl_3$ test solution.

Evaluation Summary:

- a high IEC composed of weak and strong base groups with fair stability at elevated temp
- potential ease of manufacture by one-step process requiring no post-reaction to activate resin
- disadvantages - new chemistry requiring more R&D to establish feasibility.

2.7 The CE-1 Copolymer: System 7

The CE-1 ion exchange resin represents a third example of a self-crosslinked linear copolymer system. In this case, however, only a single vinyl monomer is used with an alkyl diamine providing the needed crosslink segment. The CE-1 resin is prepared by the bulk polymerization of a linear vinyl monomer (VBC) and ethylene diamine (EDA) in isobutanol with heat and azobisisobutyronitrile initiator. The resin structure consists of a vinyl backbone crosslinked by a dibenzylaminoethyl chain resulting in two secondary amine sites.



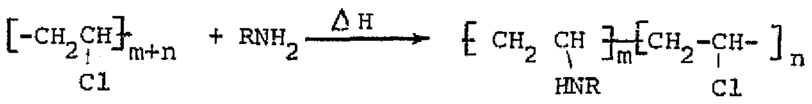
A highly stable IEC was obtained in the 4.8-5.0 meq/dgr range. The polymer showed no change in IEC or water content after 1054 hours in $FeCl_3$ test solution (1 N HCl) at 80°C, which indicated a very stable IEC group and resin matrix. A major drawback in this polymer system was the inability to synthesize a large enough area in a pinhole free film for testing of transport properties.

Evaluation Summary:

- high IEC in region of 5.0 meq/dgr which is stable at 80° C
- resin matrix appears to be physically stable at elevated temp
- potential ease of manufacture by one step bulk polymerization requiring no post reaction to activate resin
- disadvantage - new chemistry requiring further R&D to perfect

2.8 Membranes by Amination of Polyvinylchloride: Systems 8 and 9

The literature reports (Refs.35 and 37) that weak base ion exchange materials have been synthesized by direct amination of vinyl chloride polymers. Conversion of the weak base amines to higher amines and quaternary groups can be accomplished by progressive alkylation of the nitrogen radical with a suitable alkylating agent or by direct reaction with a tertiary amine. Crosslinking has also been effected by use of polyamine reagents.



$$[-CH_2\underset{Cl}{CH}]_{m+n} + RNH_2 \xrightarrow{\Delta H} [CH_2\ \underset{HNR}{CH}]_m[CH_2-\underset{Cl}{CH}-]_n$$

PVC film has a good rating for resistance to strong aqueous acids and temperatures up to 90° C.

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Two approaches to membrane fabrication were tried:

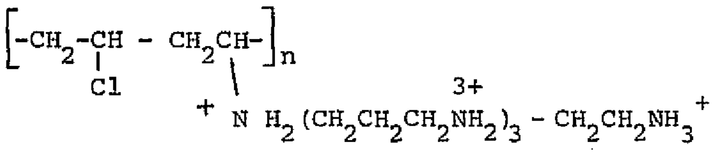
(a) Heterogenous amination of commercial PVC film;

(b) Homogenous amination of dissolved PVC followed by solvent casting the film from the reaction solution.

The former reaction (a) produced a number of promising and useful membranes represented by the membrane series VCl-TP1 to VCl-TP8 and 8X. Reaction (b) did not result in any acceptable film product. These were G1-27 to G4-27.

(a) The VCl-TP Series Membranes: System 8

The VCl-TP membranes are prepared by the direct amination of commercial 8 mil PVC grade C-255 (Dayco Co.) using tetraethylenepentamine (TEPA) at elevated temperatures. The polymer structure as prepared consists of a chlorovinyl backbone with pendant polyethyl polyamine groups consisting of secondary and primary amines (possibly tertiary also).



$$\left[-CH_2-\underset{Cl}{CH} - CH_2CH-\right]_n \quad {}^{+}N\,H_2(CH_2CH_2CH_2NH_2)_3^{3+} - CH_2CH_2NH_3^{+}$$

The reaction produces strong flexible films slightly thicker than 8 mils with exclusively weak base capacity. The extreme pliability of the film as prepared indicates little or no crosslinking. The IEC and water content were dependent on the time and temperature of the amination reaction. The range of properties obtained were IEC, 1.7 to 4.3 meq/dgr H_2O, 29 to 49% (Table 6).

The most promising film VCl-TP8 was produced at a temperature of 50° C and a reaction time of 48 hours in 100% TEPA. It was found that exposure of the membrane to 80° C temperature in $FeCl_3$ test solution resulted in a palpable stiffening of the film and a measurable tightening of the internal porosity or polymer structure evidenced by substantial loss of gel water (43-27%) and large decrease in the Fe permeation, P^{+}_{Fe} , to a low favorable level (11.7 - 0.27 mg Fe/mF).

The membrane alteration was accompanied by little or no change in resistivity (ρ^{c}) but an initial and large decline in IEC. Stability immersion tests (Table 3) in 2M $CrCl_3$, 1 N HCl at 80° C showed that the major loss in the original IEC of 2.75 meq/dgr occurred in the first 300 hrs of solution contact and achieved a stable value of 1.8 meq/dgr after 800 hrs.

The performance of the membrane in $FeCl_3$ test solution (at 80° C) was not as favorable. By 1010 hours of immersion time the IEC had declined to 1.2 meq/dgr, but here as in the Cr_2Cl_3 solution the rate of IEC loss was sharply reduced. In both cases the electrical resistance as measured by contact probes did not increase and the H_2O content after its initial decline did not change.

In both solutions the VCl-TP8 membrane tended to darken and become more brittle but still retained enough pliability to be handled and used. We interpret the stiffening as the result of progressive cross-linking of the PVC matrix produced by the continuing condensation of the pendant polyamine groups with adjacent PVC polymer chains. NASA-Lewis has reported very favorable redox cell current density performance (at room temp) for the VCl-TP8X heat treated membrane.

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The CD was 26 ASF, the highest thus far obtained from the candidate membrane series (CD for the 103QZL = 16 ASF). The Fe permeation was still too high relative to other candidate membranes.

The VCl-TP membrane system as presently manufactured shows good promise for redox cell operation. However further research and development would be needed to optimize its transfer properties and IEC stability. Important factors needing study are:

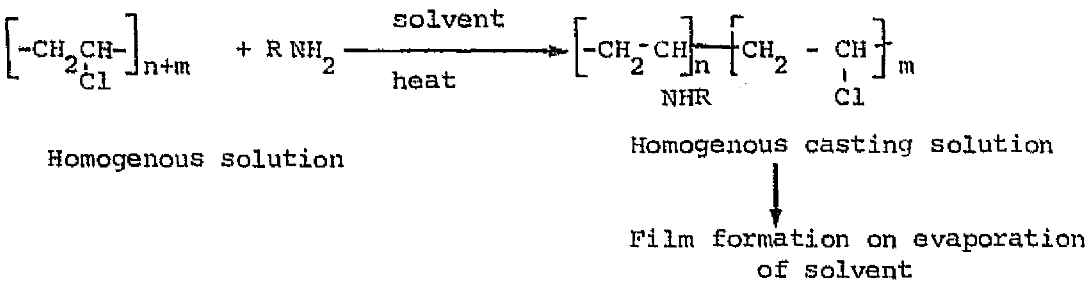
- investigate commercial PVC film of variable plasticizer content down to 2 mil gages;
- investigate reactive polyamino compounds for improved stability;
- investigate surface treatment of film for transport control.

Evaluation Summary:

- strong pliable film which can be stored dry
- low stable resistivity providing high operational current density in redox cell
- reduction in resistance possible by use of 2 mil film
- ease of manufacture by direct amination
- membrane size not limited
- good potential for low cost membrane because of cheap starting materials and possible adaptation to continuous manufacturing process
- disadvantages : requires further development to reduce cation transfer.

(b) The G1-27 to G4-27 Polymers; System 9

The second approach tried for the synthesis of a PVC membrane was the amination of dissolved PVC and casting the film from the reaction solution.



$$\left[-CH_2\underset{Cl}{CH}-\right]_{n+m} + RNH_2 \xrightarrow[\text{heat}]{\text{solvent}} \left[-CH_2-\underset{NHR}{CH}\right]_n\left[CH_2-\underset{Cl}{CH}\right]_m$$

The G1 to G4-27 polymers represent a series of films prepared by the reaction of tetraethylene pentamine (TEPA) with a 5% solution of PVC (GEON 99 - Goodrich Co.) in a mixed solvent composed of 5 parts tetrahydrofuran (THF) and 4 parts dimethylformanide (DMF). The reaction conditions were 25° C for 64 hours and 70° C for 2, 4 and 6.5 hours. All reaction solutions were cast on glass plate and film formation occurred on evaporation of the solvent.

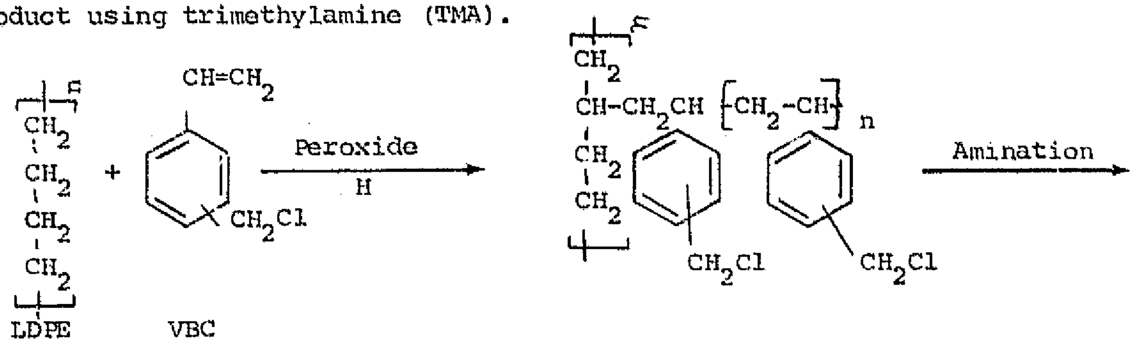
The films obtained had poor physical strength and integrity or inadequate IEC (Table 7). No further effort was expended on this approach. A possible advantage of this system is the attainment of high IEC as a result of the homogenous reaction conditions which provides less hindrance to the condensation reaction.

2.9 PV8-T49 and PV7-8T49 Membranes: System 10

The process for making ion exchange membranes by grafting styrene monomer to low density polyethylene (LDPE) film is a well known art in the field of membrane technology.

A graft copolymer consists of a high molecular weight backbone to which a second polymer is attached at intervals along the chain. The manufacture involves swelling the film with the monomer solution containing a free radical initiator such as benzoylperoxide and a small fraction of crosslinker (DVB) to create a fixed polymer network. Fine control of the proper reaction temperature and good stirring are essential conditions. After the charge has partially polymerized, the film is withdrawn wiped free of polymeric material adhering to surface, and cured at elevated temperature. Active groups are then attached to the aromatic polymer by further chemical reactions.

The PV3-8 series are candidate membranes prepared by the graft copolymerization of VBC to LDPE film followed by amination of the grafted product using trimethylamine (TMA).



The method of manufacture was similar to that described above. The reaction charge contained VBC, 0.25% in DVB, and 0.15% benzoyl peroxide initiator. The reaction temperature was maintained at 80-85° C for a period of 2 hrs. The most successful membranes were made using a 20 mil LDPE (Tenite #1830) film which had been previously crosslinked by an irradiation dose of 21 megarads. Previous attempts with conventional LDPE film were unsuccessful due to difficulty in finding proper temperature and initiator conditions .

A suitable reaction temperature for VBC polymerization was about 10-15° C higher than had been previously the experience for successful styrene graft polymerization.

The crosslinked LDPE film had the advantage of being swellable but not soluble in the monomer solution thereby allowing for less critical control of the reaction temp (Table 8).

The IEC and water contents were a function of the degree of graft copolymerization. The PV8-T49 membrane with a graft time of 2 hrs produced a strong uniform film having an IEC = 2.1 meq/dgr and a water content of 32%.

The PV7-8T49 membrane was graft copolymerized twice using two separate reactions each 2 hrs in duration. This increased the grafted material producing a moderately strong highly swelled film having an IEC= 3.4 meq/dgr and a water content of 47%.

The Fe permeation P^{+}_{Fe} of the PV8-T49 was very high (11.7 mg Fe/mF) and indicated a very open or porous structure. Because of the high porosity no further testing was done on this membrane system.

Possible synthesis modification for improvement in transfer properties would be in the direction of surface treatment to reduce film's operational porosity.

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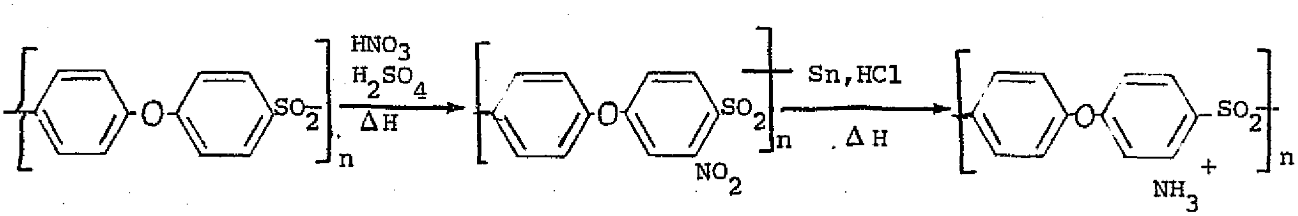
Evaluation Summary:

- strong flexible film
- should have good chemical and thermal resistance
- LDPE films are available in 1 mil gage
- potential for improvement in electrochemical properties requires more investigation
- ease of manufacture and low cost possible adaptation to continuous manufacturing process and cheap sheeting material
- may be stored dry.

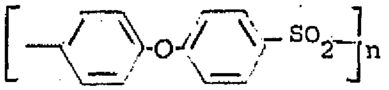
2.10 Polysulfone Cast Films: System 11

Polysulfones are high molecular weight linear thermoplastic polymers consisting of aryl units linked by oxygen and sulfone groups. This molecular configuration gives them good resistance to oxidative attack and strength at high temperatures. Polysulfones are rated usable up to 260° C and are highly resistant to chemical attack by aqueous acids and bases, and many organic compounds.

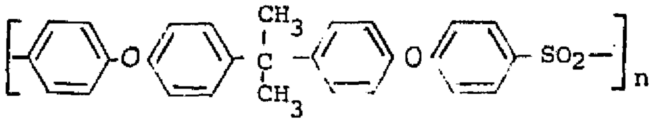
Because of these favorable properties it was proposed to utilize the polysulfone polymers as anion exchange membrane substrate to which active exchange sites could be affixed by a series of suitable chemical reactions. The proposed process involved the introduction of nitro groups (NO_2) by the homogenous nitration of the dissolved polymer followed by the reduction of these groups to amines and possibly by further reaction to alkyl substituted amines.



Two structurally different polysulfones were considered, "Astral-360" (3M Co.) and Polysulfone P-3500 (Union Carbide Co.).



ASTREL 360



Polysulfone P-3500

The synthesis of this ion exchange polymer system was not successful. Although nitrated solids were obtained containing sufficient amounts of nitrogen, no films or end products were produced which exhibited ion exchange properties or electrical conductance in acid solution.

Conventional nitration and reduction procedures for aromatic compounds were utilized. A typical nitration consisted of the addition (dropwise) of a 1:1 molal mixture of concentrated nitric acid and concentrated sulfuric acid to 10% polysulfone in chloroform(CF) solvent(nitro-benzene(NB) and dimethylformanide (DMF) solvents were also tried). The reaction solution was maintained at reflux temperature for CF and at 130-150° C for the high boiling solvents with vigorous stirring. The nitration reactions yielded yellow solids with nitrogen contents in the range of 0.4 to 4.67%, the latter being equivalent to a theoretical yield of 3.4 meq/dgr if converted 100% to the amine. The solids containing high N content were soluble in DMF, NB and CF but films cast from these solutions were non-cohesive and granular.

Several reduction reactions were attempted using finely divided tin or iron in hydrochloric acid. The products from these reactions showed no IEC or film forming character.

Evaluation Summary:

- base polymer attractive with regard to oxidative and thermal stability;
- reaction system tried does not appear feasible.

2.11 NAFION XR-475 - Thorium Membrane: System 12

It was proposed that a multi-valent positive counterion could impart stable anionic characteristics to a cation exchange resin by swamping the fixed negative charge on the resin with an excess of positive charges.

$$R\ SO_3^- + M^{+4} \longrightarrow R\ SO_3\ M^{+3}$$

A test was made to determine whether such a charge reversal group was stable in the strong acid redox environment. The cation membrane used was NAFION XR-475 (DuPont), a fluorohydrocarbon polymer with sulfonic acid exchange groups and highly resistant to heat and oxidation. Several strips of the membrane were soaked in an aqueous solution approximately 1 M in $Th(NO_3)_4$ at 60° C for 17 hours. The contact resistance of the membrane in 0.01 N NaCl increased from 81 ohms to 4000 ohms indicating considerable pick-up of Th^{+4}. However, subsequent washings with 10% H_2SO_4 (60° C) and 1 M HCl resulted in the complete recovery of its original cation exchange capacity and low contact resistance. It is apparent that strong acid readily strips off the Th^{+4} counterion. This route is not feasible for the preparation of a stable anion exchange resin and no further work along this line was done.

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2.12 Miscellaneous Candidate Membranes

Given below is a description of a number of candidate membranes listed in the data summary and in several resistivity tables but not covered in the preceding sections. All belong in the category of bulk-polymerized membranes with 4 oz dynel fabric support. They were not subject to further testing because of their similarity to the selected candidate membranes or had less favorable properties.

1. 103PZL - A standard commercial anion membrane manufactured by Ionics, Inc., consisting of a VBC-DVB copolymer substrate post aminated with TMA. Belongs to the 103QZL membrane system but has higher porosity.

2. B1L Series - Four membranes in this group consist of VBC-EGDM copolymer substrate and a variety of amine substituents. These belong to the same polymer system as the B2L-TP95 membranes but have a higher crosslink content and lower IEC.

   (a) B1L-D8, B1L-D37 - post reacted with dimethylamine (DMA) to give a dimethylbenzylamine (tertiary amine) exchange group.

   (b) B1L-DT19 - post reacted with diethylenetriamine (DETA) to give an exchange group with three weak base amine sites identical to those in the B2L-T95.

   (c) B1L-T19 - post reacted to trimethylbenzyl quaternary amine exchange site.

3. B2L Series - Three membranes belong to the same membrane substrate system as the B2L-DT95 VBC-EGDM copolymer aminated with several different amines.

   (a) B2L-D37 - aminated with DMA giving same exchange group as in 2(a);

   (b) B2L-DT19 - identical to the B2L-DT95 membrane;

   (c) B2L-T19 - aminated with TMA and has same ion exchange group as in 2(c).

3.0 MEMBRANE SYNTHESIS - NON-POLYMERIZING SOLVENT VARIATIONS

The majority of candidate membranes have been prepared through bulk polymerization of the liquid monomers in the presence of a non-polymerizing solvent (NP) with a free radical initiator and heat. This includes the membranes with the identification code prefix of B1L, B2L, A3L, A4L, C1L, CD1L, 103QZL, 103 PZL, CE, and CP2L.

In these polymer systems the ability of the membrane to screen out or exclude ions and molecules of differing sizes is critically affected by the fraction of the solvent used as the non-polymerizing component of the monomer mixture. Spaces or pores are formed in the polymer structure by the solvent molecules as the polymerizing mass forms around and traps them. The solvent molecules are eventually replaced by H_2O. The membrane acquires a hydrophilic character by the addition of ionizable groups. Our experience in membrane synthesis has shown that a large fraction of NP solvent in the order of 60-70 percent produces porous membranes which exhibit low ionic selectivity and high permeability to large unionized molecules,such as sucrose. At NP solvent fractions in the 30-40 percent region the resultant films tend to sharply reduce sucrose transfer and improve in ion selectivity.

The membrane pore size is not only affected by the quantity of solvent used but also by the size of the solvent molecule. In addition the membrane's physical properties such as brittleness, flexibility, hardness are influenced by the solvent component.

In the syntheses reported here very substantial reductions in Fe permeation (P^{+}_{Fe}) were achieved with a relatively small decrease in the NP solvent fraction of the monomer charge. (Table 9). For the A3L series a decrease in the solvent fraction from 0.40 to 0.35 produced a very dramatic drop in P^{+}_{Fe} from 1.43 to 0.066 mg Fe/mF. A similar effect was demonstrated for the other candidate systems.

A lower H_2O content or porosity tended to increase the electrical resistance. However, maintaining high IEC in the membrane served to counteract the unfavorable conductance effect. An advantage of the bulk polymerization system is the ability to vary the NP solvent fraction independently of the ionogenic monomer fraction thus allowing the same or higher amounts of active ingredients to be incorporated into the film.

Further reduction in Fe permeation could be reached by determining and refining the practical limits of solvent species and concentrations. Maintaining the highest possible IEC also contributes to good membrane selectivity. By combining high IEC with low H_2O content, the fixed charge density or interstitial molality (I_M) of the resin can be increased, thereby improving the anion membrane's effectiveness for excluding cations. The interstitial molality, I_M , expressed in terms of meq of exchange groups per gram resin water content (meq/g H_2O) has been calculated for a series of candidate anion membranes and shows fairly good correlation with Fe permeation (Table 10).

4.0 MEMBRANE TESTING

Specimens prepared in this program were screened and evaluated systematically starting with visual and manual inspection of the new film. The preliminary tests included qualitative estimates and observations of the films' gross characteristics such as handling strength, degree of flexibility, quality of the surface coating, presence of cracks, blisters. spalling and leakage.

When a specimen qualified for further consideration, it was characterized by a variety of quantitative analyses well known in the art. These included analyses for ion exchange capacity (IEC) of weak and strong base groups, resin water content, film thickness, electrical resistance by several methods (liquid junction and contact probes); and, where indicated, a test for permeation of ferric ion (Fe^{+3}) at a specified current density. Analytical details are described in the appendices.

The above qualitative and quantitative analyses were also utilized to monitor long term oxidative and thermal stability of selected candidate membranes in a redox cell environment at elevated temperature.

Priority was given to the determination of the stability of the ion exchange groups and supporting resin matrix of the various candidate membrane systems showing initial favorable physical and chemical characteristics as manufactured.

Potential for improvement of the electrochemical properties of the candidate membrane was explored and a series of second generation improved membranes were prepared and evaluated.

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A summary of membrane resistivities measured by the liquid junction and contact probe methods is given in Table 11.

4.1 Membrane Resistivity Change in Ferric Chloride Solution

When an anion membrane is immersed in aqueous $FeCl_3$ the electrical resistivity of the membrane tends to increase to a higher value in a short period of time. NASA-Lewis proposed using this resistance effect as a screening test for candidate membranes. Using a procedure suggested by NASA-Lewis, a group of candidate membranes were tested for change in resistance in $FeCl_3$.

The test apparatus was the conductivity cell described in Appendix IIIa with the following configuration:

Electrode/2M$FeCl_3$, 1 N HCl/membrane/1NHCl/electrode

Membrane samples were fixed between the two half cells and allowed to stand in contact with the 2M $FeCl_3$, 1N HCl in one compartment and 1N HCl in the other compartment for a period of 18 hrs at ambient temperature. Resistance values were taken initially and at the 18 hour point. The results are summarized in Table 12.

Most membranes showed an increase in resistivity. This effect may be due to the exchange of chloride ions for the less mobile and larger ionic species $FeCl_4^-$. The variable resistivity increase observed in the candidate membranes could result from variable penetration into the resin by the large complex anion, its extent influenced by factors of resin porosity and ion exchange group affinity for $FeCl_4^-$.

The data indicates that resistance change as represented by the ratio ρ_f/ρ_o (ρ_f = final resistivity, ρ_o = initial resistivity) could be related to the type of amino exchange group present (Table 13).

The smallest increase and the two cases of decrease in resistivity were obtained with polymers bearing acidified primary and secondary amino groups. The ρ_f/ρ_o range for this set was 0.79 to 1.56 with the lowest region represented by membranes having the greatest number of secondary amine groups.

The PVC membranes VCl-TP5 and VCl-TP6 were the only membranes showing a resistivity decrease with time. Part of this decrease with time may be due to greater diffusion of H^+ because of the high membrane porosities.

The membranes possessing tertiary amino exchange groups showed a relatively large change in resistivity, ρ_f/ρ_o, in the narrow range of 1.90 - 2.20. The greatest change in resistivity was given by the 103QZL which contains a trimethyl benzyl quaternary ammonium group. The ρ_f/ρ_o for the strong base group was 1.68 - 3.18.

4.2 Membrane Permeability Testing

An ideal membrane separator for the proposed redox cell would be one which was highly conductive but permitted little or no transfer of Fe^{+3}, Fe^{+2}, Cr^{+2}, Cr^{+3}, Ti^{+3} or Ti^{+4} in either the charging or discharging mode of operation.

An apparatus and a procedure were developed to evaluate the candidate anion membranes for their relative permeability using Fe^{+3} as the model transfer species. The procedure consisted of simulating a redox half cell operation in the charge mode with a flowing $FeCl_3$ solution on the anodic side of the membrane and a static collection cell on the cathodic side to capture the migrating Fe^{+3} for analysis. The permeability factor P^+_{Fe} represents the Fe^{+3} in mg transferred per millifarady of electrical energy applied.

A detailed description of the permeation apparatus and procedure is given in Appendix IV.

The initial data obtained in the permeation tests indicated an extremely wide variation in the ability of the various candidate membrane to exclude Fe^{+3}. (Table 4 , Fig. 1.) The highest and lowest Fe permeation factor P^+_{Fe} differed by an unusually large factor of 3×10^3 with the 103PZL at 40 mg Fe/mF and the PVC membrane VCl-TP-4 at .013 mg Fe/mF.

The permeation test proved valuable for confirming the effects of various synthesis modifications intended to reduce membrane porosity and the subsequent improvements in Fe^{+3} exclusion. The reduction of formula solvent in a number of bulk polymerized membranes produced substantial reductions in Fe transfer (Table 9).

The Fe^{+3} permeation procedure also provided a sensitive test for detecting (and confirming) internal structural changes in the resin. The measurable increase in P^+_{Fe} from .02 to .09 mg Fe/mF, for the B2L-DT95 membrane after 520 hrs in $CrCl_3$ at 80° C (Table 3) was consistent with other data, i.e. increase in H_2O content and decrease in resistivity; all indicative of a loosening of the polymer structure by a small amount of EGDM hydrolysis. The membrane showed no obvious or visible signs of resin deterioration.

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When the test cell was operated in the discharge mode, reversing electrical polarity, the Fe^{+3} transfer declined by a large factor. The 103QZL membrane showed a P^{+}_{Fe} of .024 mg Fe/mF in the discharge mode of cell operation and 1.0 mg Fe/mF in the charging direction. The large difference in Fe^{+3} transfer is probably due to several factors. The concentration of Fe^{+3} and its positive complexes $FeCl^{+2}$, $FeCl_2^{+}$ is much greater than the concentration of $FeCl_4^{-}$ and the bulkier size of the anion complex $FeCl_4^{-}$ makes it more difficult to enter the resin pore structure.

The charging mode of cell operation offers a more valuable screening test for the candidate anion membranes. The charging polarity imposes a more rigorous test for membrane selectivity in the redox cell environment and represents the maximum Fe^{+3} loss permitted by the membrane.

4.3 Membrane Immersion Stability Test

The chemical and thermal stability of the ion exchange group and supporting structure in the redox cell environment is a primary consideration in the screening and selection of a suitable anion membrane for the redox cell application. Degradation and loss of the ion exchange group could result in a progressive increase in electrical resistance and decrease in ion selectivity of the membrane. Degradation of the polymer backbone or crosslinkages could lead to weakening of the resin structure, increase in porosity or formation of holes, and consequent gross leakage of the redox cell chemicals.

Because little empirical data was available on membrane stability in the relevant solutions, priority was given to stability testing of the candidate ion exchange systems and that synthesis work aimed at optimizing structural, porosity, and transport characteristics of the membranes was deferred to a later part of the program.

(a). Procedure. The stability of the candidate anion membranes was tested by immersion of membrane samples in $FeCl_3$ and $CrCl_3$ solutions at 80° C and analysis of membrane properties at various intervals for a total exposure time of about 1000 hrs. Sections of membrane approximately 2-1/2" x 3" were suspended in the solutions separated by polyethylene screen spacers to provide good solution-membrane contact.

The solutions were 2M in the metallic ion and 1M in HCl. The test vessel was a glass jar with a teflon lined screw cap seal and maintained at 80° C in a constant temperature forced draft oven.

The analyses included:

a. Strong and weak base ion exchange capacities.

b. % water.

c. Electrical resistance taken at 0.1N HCl with contact probes (earlier data was taken at pH4.)

d. Description of gross resin condition.

e. Leak test for pinhole defects by use of non-staining dye.

f. Fe permeation whenever relevant.

Most of the strong and weak base amino exchange groups showed very good stability exhibiting little or no loss in IEC with immersion time. The IEC's obtained were in the range of 2.3 to 5.4 meq/dgr and included examples of primary, secondary, tertiary, and quaternary amines. (Table 3).

The aminated PVC film (VCl-TP8) was the sole membrane type which lost substantial IEC in the test environment. The major IEC loss occurred early in the test period, but the rate of IEC decline tended to drop sharply with time and stabilized at a lower but acceptable level.

The data showed a wide variation in the stability of the supporting polymer structure of the candidate membranes. Two indicators were used as a measure of relative polymer stability (1) the quantitative increase in the water content, (2) qualitative estimate of resin erosion or visible film deterioration.

Break up or loosening of a crosslinked polymer network by chemical attack and cleavage of the polymer backbone or crosslinks results in increased swelling or solvent absorption in the polymer and also in obvious deterioration in resin strength if the polymer degradation is severe.

On this basis, the most stable membrane was the 103QZL. Its polymer structure consists of a vinyl backbone and vinyl aromatic crosslinks. No resin erosion, gross change, or increase in H_2O content was observed at any time in the $FeCl_3$ or $CrCl_3$ test environment at 80° C. The 103QZL membrane sample which functioned for 6000 hrs in a $FeCl_3$-$TiCl_3$ redox cell at NASA-Lewis also showed no obvious sign of resin deterioration although there was some indication of fouling or plugging of the surface pore structure. The membrane showed a substantial decrease in Fe permeation and also a moderate loss in IEC, water content, and electrical conductance.

Membranes containing ethylene glycol dimethacrylate (EGDM) as the crosslinking element exhibited only a fair polymer stability to $CrCl_3$ under

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the drastic conditions of the testing. These were the membranes A3L-18, A3L-96, B2L-TP95, and C1L-96. Their polymer structure consists of a vinyl backbone and a diester crosslinking chain. As the IEC remained constant or even increased, it was evident that the EGDM segment was being hydrolyzed and cleaved in varying amounts.

Most of the EGDM membranes showed a 10 to 20 percent increase in H_2O content but little or no resin erosion or swelling. The membrane most seriously affected was the A3L-18, a copolymer of 2-vinyl pyridine and EGDM. The membrane increased 53% in H_2O content accompanied by severe swelling, leakage and loss of film rigidity after 570 hr exposure to 2M $CrCl_3$, 1M HCl solution at 80° C. The marked increase in IEC indicated a leaching of non-ionic solids from the polymer (probably ethylene glycol).

Although some membrane types with an EGDM component showed signs of only small decomposition in the strong acid and high temperature test conditions, and could probably offer reasonable durability in a less aggressive environment, a more chemically resistant crosslinking agent than EGDM is desired for this project. High purity commercial DVB which contains 72-80 percent as DVB crosslinking monomer would be a feasible substitute for EGDM, imparting good stability to the membrane without serious loss of IEC or alteration of other membrane properties.

5.0 CONCLUSIONS

Most of the strong and weak base amino exchange groups have shown good stability in the acid and high temperature test environments.

Divinylbenzene was found to be the most stable crosslink agent for membranes of the bulk polymerized type, especially in the presence of chromic ions.

Post-treatment of aminated PVC film using heat (80° C) in a redox electrolyte produced a lower porosity membrane with improved ability to exclude Fe^{+3}. The film was strong, flexible and showed no decline in resistivity after the 1000 hr immersion stability test.

Improvement in Fe^{+3} exclusion in candidate anion membranes prepared by bulk polymerization can be accomplished by reducing the non-polymerizing solvent in the formulation and also by increasing the IEC.

Ethylene glycol dimethacrylate (EGDM) appears unsuitable as a crosslink monomer for polymers exposed to strong acid and chromic-ions in a high temperature (80° C) oxidizing environment. Membranes containing EGDM have shown only fair polymer stability in the test solutions. However EGDM may be suitable at lower temperatures even in the presence of Cr^{+3}.

Substitution of high purity commercial DVB (72%) for EGDM is feasible and should impart good resin life to bulk polymerized membranes without significant alteration in ion transfer properties.

The 103QZL membrane sample which functioned for 6000 hrs in a $FeCl_3$-$TiCl_3$ redox cell at NASA-Lewis showed no sign of resin deterioration however some fouling or plugging of the pore structure was indicated by a large decrease in Fe permeation value and moderate loss in IEC, water content, and electrical conductance.

Life testing has shown that it is indeed feasible to prepare membranes capable of use in a redox cell of NASA-Lewis type which will tolerate 80° C and the presence of highly oxidizing transition metal ions.

6.0 RECOMMENDATIONS FOR FURTHER WORK

This contract has been concerned with a large membrane screening program which has produced a minimum of four new anion permselective membranes. These have been shown to be excellent candidates for use in the iron-titanium or iron chromium redox battery. However, none of these new and novel membrane types have in any sense been optimized in terms of the following:

a. minimal cation transfer across membrane (formulation variations);

b. minimal resistivity (film thickness reduction);

c. long term high temperature stability to chromic ions (use of 72% divinylbenzene)

We recommend that each type of new membrane synthesized be optimized in each of the categories listed above so as to guarantee meaningful testing of substrates that will function in the redox cell in terms of:

a). Near zero metal ion transport across the anion membrane;

b). 80° C long term life capability;

c). resistivity approaching that of its acid environment;

d). ability to manufacture membranes in terms of many square feet;

e). good reproducibility of any membrane prepared.

All of the above recommendations would be carried with cooperative testing at NASA-Lewis as was done in the present contract.

A program of two to three man years is recommended.

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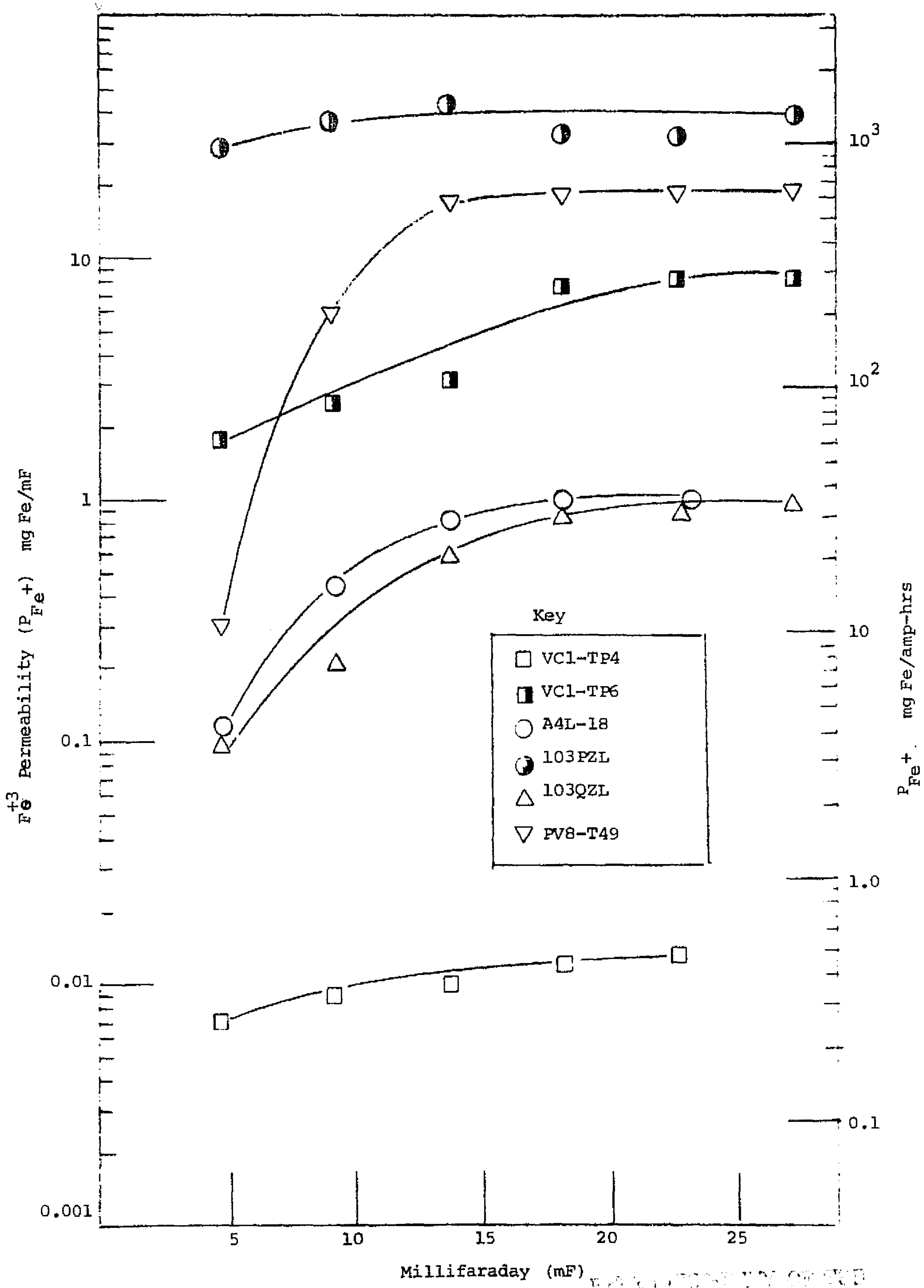
SYMBOLS

	Definition	units
ρ^J	Resistivity by liquid junction method	ohm-cm
R_ρ^J	Area resistance by liquid junction method	ohm-cm^2
ρ^c	Resistivity by contact probe method	ohm-cm
R_ρ^c	Area resistance by contact probe method	ohm-cm^2
P_{Fe}^+	Permeation factor for Fe in the charging mode	mg Fe/mF
mF	millifaraday	96.5×10^3 ma-sec
IEC	Ion exchange capacity	meq/dry gram resin
I_M	Interstitial molality	meq/gm H_2O

FIG. 1 Fe^{+3} Permeability of Various Experimental Anion Membranes



.MEMBRANE CONDUCTIVITY APPARATUS

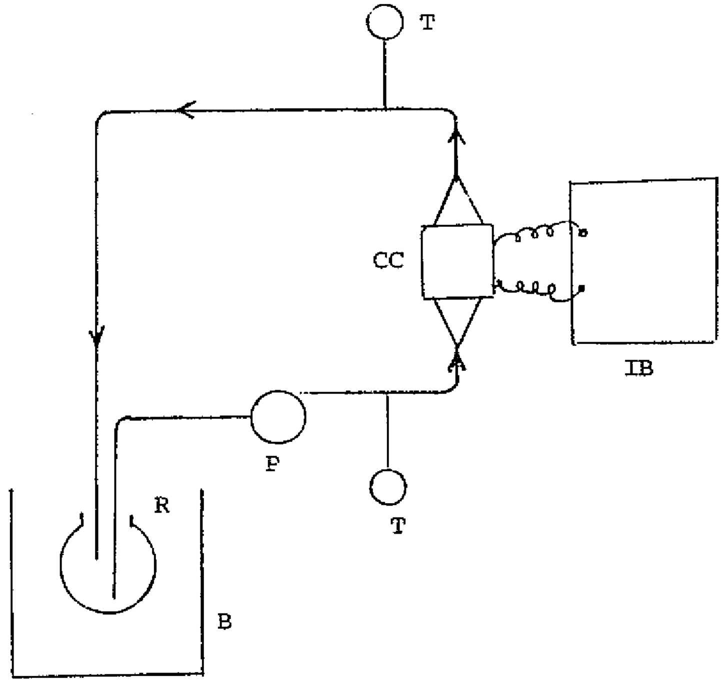


FIG.A1 -- FLOW DIAGRAM

CC, conductivity cell; IB, impedance bridge; P, pump; T, thermometer; R, solution reservoir; B, constant temp.bath

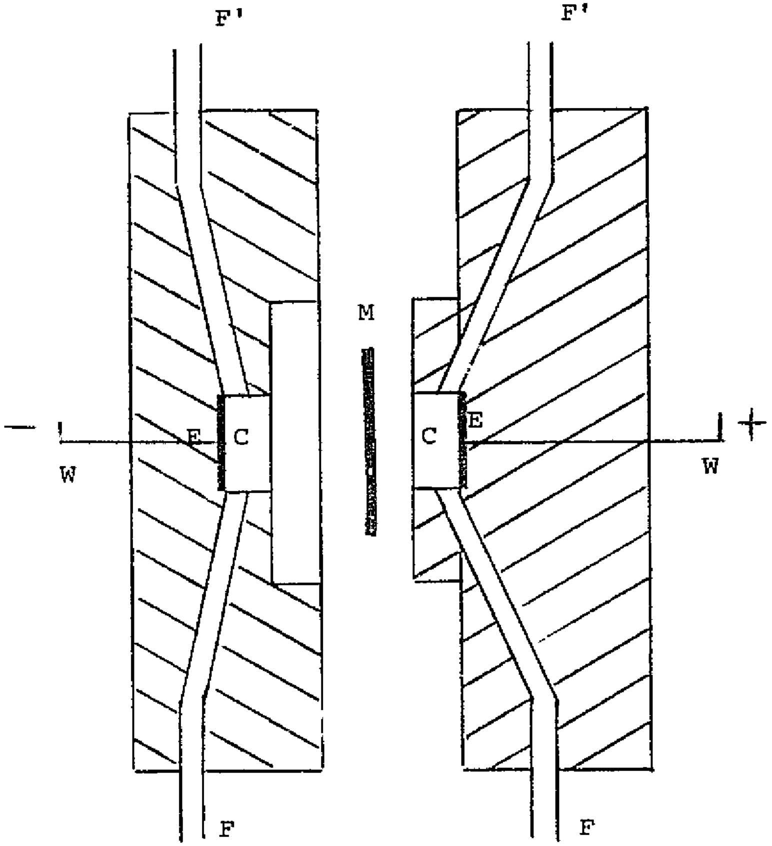
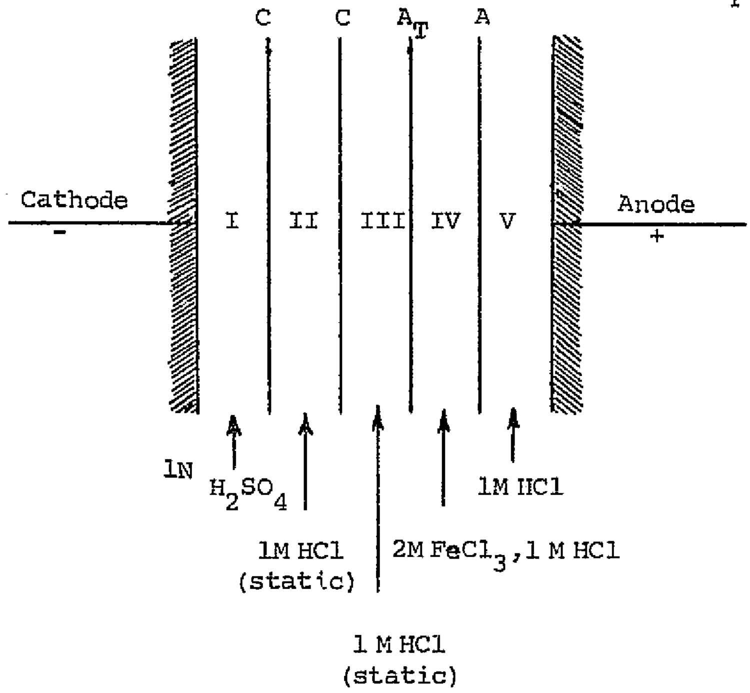


FIG.A2 -- CONDUCTIVITY CELL (CROSS SECTION)

C, solution compartment; M, membrane; E, platinized platinum electrode; W, electrode connector; F, F', inlet, outlet

Figure A3 PERMEABILITY TEST CELL DIAGRAM

C, cation membrane; A, anion membrane; A_T, test membrane



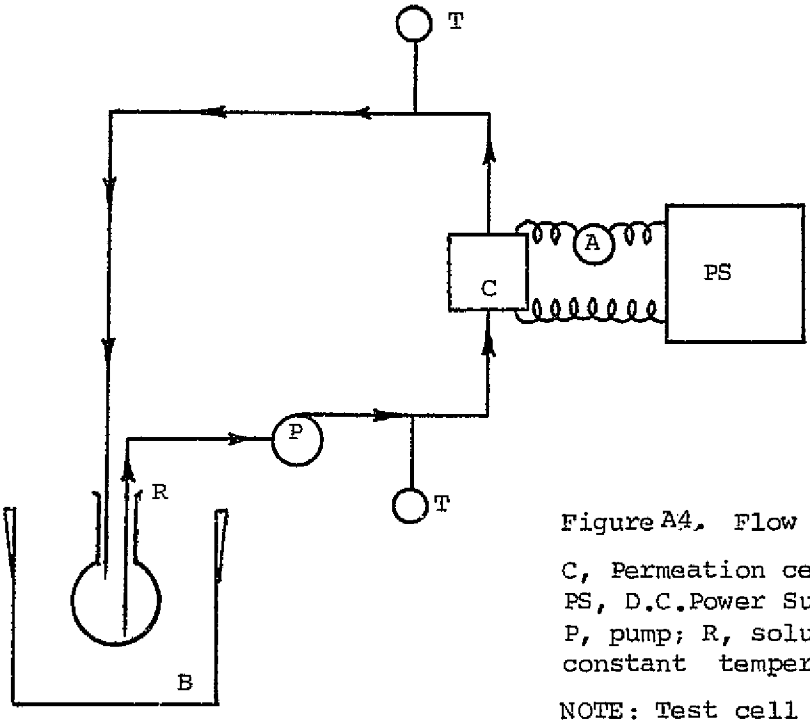


Figure A4. Flow Diagram

C, Permeation cell; T, thermometer; PS, D.C.Power Supply; A, ammeter; P, pump; R, solution reservoir; B, constant temperature bath

NOTE: Test cell utilizes three pumps, with separate streams to compartments I, IV and V.

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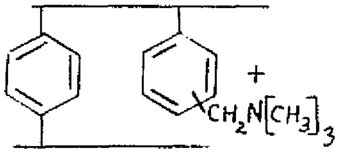
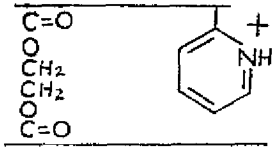
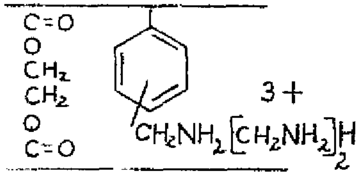
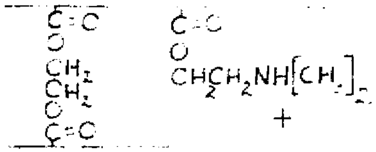
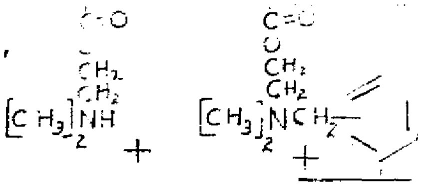
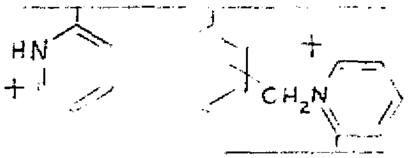
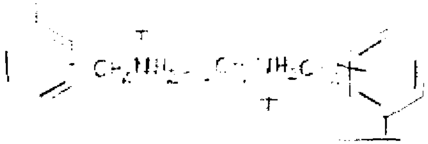
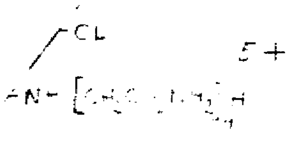
Table 1: Candidate Anion Membranes: Glossary and Evaluation

Membrane (Backing)	Polymer Composition	Polymer Structure [1]	Functional IEC Group (meq/dgr)	Thermal & Chemical Stability @ 80° C in redox solution	Permeability to Fe (P_{Fe}^{+})	Remarks
103QZL (dynel fabric)	Vinylbenzylchloride, divinylbenzene copolymer post aminated with trimethylamine		benzyltrimethyl ammonium chloride quaternary amine (2.1)	IEC - very stable resin-very stable	low, decreases with time in redox soln.	Good candidate, P_{Fe}^{+} can be reduced by decreasing solvent in formulation; good potential for improvement
A3L-18 (dynel fabric)	2-vinyl pyridine ethylene glycol dimethacrylate copolymer		pyridinium HCl tert. amine (3.1)	IEC - stable resin-moderate erosion, stable at ambient temps	low	possible candidate, resin stability with 72% DVB- good potential for improvement
A4L-18 (dynel fabric)	as above	as above	as above (4.3)	IEC-stable resin-severe erosion, stable at ambient temps	low	as above
A3L-96 (dynel fabric)	as above	as above	as above (3.1)	IEC-stable resin-degrades rapidly in $CrCl_3$, longer life at moderate temps	very low	as above
B2L-DT95 (dynel fabric)	vinylbenzyl chloride ethylene glycol dimethacrylate copolymer post aminated with diethylene triamine		diethylenetriamine HCl Sec., prim. amine (5.4)	IEC-stable resin- fair stability, no resin erosion at 1300 hrs.	lowest P_{Fe}^{+}	Recommended candidate, highest IEC, resin stability with 72% DVB, good potential for improvement

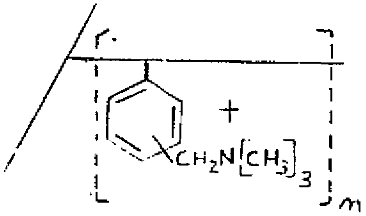
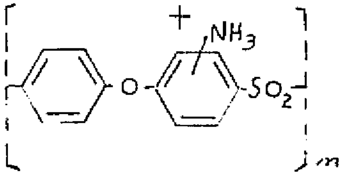
[1] Line (———) designates vinyl backbone structure

Table 1(Continued)

Membrane (Backing)	Polymer Composition	Polymer Structure[1/]	Functional IEC Group(meq/dgr)	Thermal & Chemical Stability @ 80°C in redox solution	Permeability to Fe (P_{Fe}^{+})	Remarks
C1L-96 (dynel fabric)	dimethylamino-ethylmethacrylate, ethylene glycol dimethacrylate copolymer		dimethylethyl-amine HCl tertiary amine (3.2)	IEC-very stable resin - fair stability - erosion moderate	very low	possible candidate requires more R&D
CD1L-96 (dynel fabric)	dimethylamino-ethylmethacrylate, vinylbenzyl chloride		dimethylethyl-amine HCl and benzyl derivative; tertiary, quaternary amine (4.1)	IEC-small loss resin - fair stability erosion moderate	very low	possible candidate requires more R&D
CP26-64 (dynel fabric)	vinylbenzyl chloride, 2-vinylpyridine copolymer		tertiary and quat.pyridinium amines (4.2)	IEC - stable resin-severe erosion	film leaks	requires more R&D
CE-1 (dynel fabric)	vinylbenzyl chloride ethylene diamine copolymer		ethylene diamine HCl sec.amines (4.8)	IEC - stable resin - stable	film not homogenous leaks	requires more R&D
VCl-TP8	polyvinylchloride film aminated with tetraethylene-pentamine		Tetraethylene pentamine HCl sec.,prim.amine (2.7)	IEC - decreases at 80° C , long range stability promising, film-strong	very low after 100 hr conditioning at 80° C	recommended candidat good potential for improvement
VCl-TP7B	as above	as above	as above(1.50)	IEC decreases at 80° C, IEC level too low	Low	as above

[1/] Line (——) designates vinyl backbone structure

Table 1 (Continued)

Membrane (Backing)	Polymer Composition	Polymer Structure[1]	Functional IEC Group(meq/dgr)	Thermal & Chemical Stability @ 80°C in redox solution	Permeability to Fe (P^+_{Fe})	Remarks
PV7-8T49	vinylbenzyl chloride grafted to LDPE (Irrad.), aminated with trimethyl amine		trimethylbenzyl ammonium chloride quat. amine (3.4)	not tested	high	requires more R&D
NAFION XR475-Th (Teflon)	Sulfonated fluorohydrocarbon, saturated with $Th(NO_3)_4$	$RSO_3\ Th^{+3}$	Thorium sulfonate	Acid removes Th^{+4}	not tested	Rejected
NA2R-17	Polysulfone nitrated and reduced		Phenyl-amine			Synthesis not successful

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[1] Line (——) designates vinyl backbone structure

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Table 2: DATA SUMMARY: Chemical & Physical Properties of Experimental Anion Membranes

Membrane	Polymer	Post Treatment	Weak Base IEC meq/dgr	Strong Base IEC (meq/dgr	% H_2O	Thickness (mils)	Resistivity at 25° C ρ^c (Ω-cm)	Resistivity at 25° C ρ^J (Ω-cm)	P^+_{Fe} (mg Fe/mF)	Physical Condition
103PZL	VBC-DVB	Amination $\bar{c}$ TMA	-	2.2	45.0	21		49.7	40.5	A
103QZL	VBC-DVB	Amination $\bar{c}$ TMA	-	2.34	36.6	21	151(370)	77.5	1.0	A
A3L-18	2VP-EGDM	none	3.17	-	43.3	24	110	65.3	1.43	A
A4L-18	"	"	3.28	-	45.2	24	85	59.5	1.0	A
A3L-96	"	"	3.12	-	39.8	29	154	-	0.066	
B1L-D8	VBC-EGDM	Amination $\bar{c}$ DEA	3.2		46	25	-	62.7	-	A
B1L-D37	"	" "	-		-	25	-	66.1	-	A
B1L-DT19	"	" DETA	4.6	-	39.0	26	(244)	89.5	-	A
B1L-T19	"	" TMA	-	2.9	45.1	29	(230)	40.8	-	A
B2L-D37	"	" DEA	-	-		27	-	68.6	-	A
B2L-DT19	"	" DETA	4.9	-	39.0	27	-	95.6	-	A
B2L-DT95	"	" "	5.38	-	41.9	25	145	-	0.029	A
B2L-T19	"	" TMA	-	3.1	45.2	27	-	50.6	-	A
C1L-B	DMAEMA-EGDM	none	2.7	-	44	20	-	45.9	-	A
C1L-96	" "	"	3.24	-	37.6	-	99	-	0.071	A
CD1L-56	" -VBC	"	2.22	2.07	46.8	31	(142)	47.6	0.22	A
CD1L-96	" "	"	2.00	2.08	39.8	27	72	-	0.047	B
CD1L-66Q	" "	Quaternized $\bar{c}$ DMS	-	3.41	47.2	26	(151)			B
CP2L-64	2VP-VBC	none	2.52	1.66	53.0	28	58	-	-	C
CE-1	2VP-EDA	"	4.76	-	59.1	30	76	-	-	C
VC1-TP4	PVC Film	aminated $\bar{c}$ TEPA	1.7	-	29	7.0	(405)	106	0.013	A
VC1-TP5	" "	" "	3.2	-	45	8.7	(270)	41.8	10.1	A
VC1-TP6	" "	" "	4.3	-	49	8.7	(78)	42.5	8.3	A
VC1-TP7B	" "	" "	1.53	-	28	8.5	(350)		0.41	A
VC1-TP8	PVC film	amination $\bar{c}$ TEPA	2.75	-	42.5	8.0	168	-	11.7	A
VC1-TP8X	" "	" "	1.50	-	26.5	8.0	160	-	0.27	A
PV7-8T48	LDPE film irradiated	" "	-	3.4	47	47	-	10.2	-	A
PV8-T49	"	" "		2.1	32	28	-	28.9	19.3	A
G4-27	aminated PVC Solvent cast	None		2.1	78	5.0	(910)	-	-	C

See next page for Key

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Key:

DMS - dimethyl sulfate
VBC - vinylbenzyl chloride
DVB - divinylbenzene
2VP - 2-vinyl pyridine
EGDM - ethylene glycol dimethacrylate
DMAEMA - dimethylaminoethylmethacrylate
EDA - ethylene diamine
TMA - trimethylamine
DEA - diethylamine
DETA - diethyltriamine
TEPA - tetraethylene tetra-amine

ρ^c - resistivity measured by contact probes at 0.1N HCl or (pH 4)

ρ^J - resistivity measured by liquid junction in 1.0 M HCl

P^{+}_{Fe} - Fe permeation measured in 2M $FeCl_3$, 1N HCl solution at CD = 60 ma/cm^2

Physical Condition:

A - good
B - fair
C - poor

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Table 3

Immersion Stability Test - Experimental Anion Membrane Properties

Test Solutions:
A = 2M $FeCl_3$, 1M HCl at 80°C
B = 2M $CrCl_3$, 1N HCl at 80° C
C = NASA Lewis Redox Cell Test, Fe/Ti couple in 0.5N, 6.0N HCl at R.T.

Membrane	Test Solution	Immersion Time (hrs)	Weak Base IEC (meq/dgr)	Strong Base IEC (meq/dgr)	% H_2O	Contact Resis. R^c_ρ in 0.1N HCl (ohm-cm^2)	Fe Permeation P^+_{Fe} (mgFe/mF)	Resin Condition Erosion	Resin Condition Leaks	Resin Condition Other
103-QZL	A	0	0.06	2.34	36.6	9.5	1.0	none	none	none
		119	0.08	2.28	34.4	-	-	"	"	"
		624	0.23	2.27	33.6	-	0.49	"	"	"
		1054	0.15	2.28	35.9	12.0	0.38	"	"	"
103QZL	B	0	-	2.34	36.7	9.5	1.0	none	none	none
		570	-	2.40	36.9	10.3	-	"	"	"
		1293	-	2.46	36.8	9.3	-	"	"	"
103QZL	C	0	-	2.34	36.7	9.5	1.0	none	none	none
		6000	-	1.84	32.9	12.7	0.071	"	"	dark color
A3L-18	A	0	3.17	-	43.3	6.7	1.43	none	none	-
		672	3.60	-	53.0	6.3	-	slight	slight	-
A3L-18	B	0	3.17	-	43.3	6.7	1.43	none	none	-
		503	3.78	-	60.1	3.8	-	moderate	moderate	swelled
A4L-18	A	0	4.28	-	45.2	13[1]	37	slight	none	-
		119	-	-	46.1	14[1]	-	severe	none	-
		624	4.39	-	49.2	13[1]	-	"	"	-
		1054	4.48	-	53.6	11[1]	-	"	"	-

Membrane	Test Solution	Immersion Time (hrs)	Weak Base IEC (meq/dgr)	Strong Base IEC (meq/dgr)	% H_2O	Contact Resis. R^C_Ω in 0.1N HCl (ohm-cm^2)	Fe Permeation P^+_{Fe} (mgFe/mF)	Resin Condition		
								Erosion	Leaks	Other
A3L-96	A	0	3.12	-	39.8	9.4	.066	none	none	-
		159	3.37	-	45.2	6.5	-	slight	slight	-
		672	3.66	-	48.3	6.4	-	slight	none	-
A3L-96	B	0	3.12	-	39.8	9.4	.066	none	none	-
		570	4.09	-	60.8	3.9	-	moderate	severe	swelled
		1293	4.37	-	66.6	3.6	-	"	moderate	"
B2L-DT95	A	0	5.38	-	41.9	8.0	0.029	none	none	-
		570	5.38	-	46.4	6.4	-	"	"	-
		1293	5.33	-	47.0	4.9	-	"	"	-
B2L-DT95	B	0	5.38	-	41.9	8.0	0.029	none	none	-
		570	5.32		46.2	5.5	0.089	"	"	-
C1L-96	A	0	3.24	-	37.6	6.4	0.071	none	none	-
		570	3.34	-	42.3	6.0	-	slight	"	-
		1293	3.65	-	44	5.4	-	moderate	"	stiff
C1L-96	B	0	3.24	-	37.6	6.4	0.071	none	none	-
		570	3.24	-	42.3	4.9		"	"	
		1293	3.25	-	44.2	5.4		"	"	
CD1L-96	A	0	2.15	1.90	41.8	4.9	-	none	none	-
		570	2.14	1.76	43.6	4.9	-	"	"	-
		1293	1.40	2.81	45.2	5.9	-	moderate	slight	stiffened
CD1L-96	B	0	2.15	1.90	41.8	4.9	0.047	none	none	-
		570	1.60	2.08	47.0	4.6	-	slight	"	-
		1293	2.63	1.24	50.9	4.1	-	none	"	-

Membrane	Test Solution	Immersion Time (hrs)	Weak Base IEC (meq/dgr)	Strong Base IEC (meq/dgr)	% H_2O	Contact Resis. R_Ω^c in 0.1N HCl (ohm-cm^2)	Fe Permeation P_{Fe}^+ (mgFe/mF)	Resin Condition		
								Erosion	Leaks	Other
CP2L-64	A	0	2.52	1.66	53.0	4.2, (10)[1]	-	slight	variable	
		119	-	1.42	49.6	- , (12)[1]	-	severe	severe	
		624	-	1.57	46.8	- , (11)[1]	-	"	"	
		1054	2.75	1.38	49.0	4.7, (12)[1]	-	"	"	
CE-1	A	0	4.76	-	59.1	5.7, (16)[1]	-	none	slight	
		119	-	-	59.2	- , (17)[1]	-	"	moderate	
		624	-	-	59.6	- , (18)[1]	-	"	moderate	
		1054	4.97	-	59.4	5.3, (13)[1]	-	"	"	
VC1-TP73	A	0	1.53	-	28.0	78[1]	0.41	none	none	
		119	-	-	-	39[1]	-	"	"	dark, stiff
		624	1.24	-	16.8	70[1]	.004	"	"	" "
		1054	0.86	-	22.2	12-62	.007	"	"	" "
VC1-TP8	A	0	2.75	-	42.5	3.7	11.7	none	none	-
		144	1.50	-	26.5	3.6	0.27	"	"	dark, stiff
		1010	1.18		26.8	3.9		"	"	" "
VC1-TP8	B	0	2.75	-	42.5	3.7	11.7	none	none	
		284	2.02	-	28.4	2.1	-	"	"	dark stiff
		785	1.77	-	26.5	3.1	-	"	"	" "
		1006	1.82	-	27.5	3.4	-	"	"	" "

(1) contact probe resistance taken in pH 4

Table 4: Vinylbenzyl Chloride - 2 Vinyl Pyridine Copolymer; Properties as a Function of Initiator Concentration

Initiator - AzoBisisobutyronitrile; Molar Ratio VBC/2 VP=0.5; Isobutanol - 40% by vol.

Test No.	Initiator (g/100 ml)	IEC Total (meq/dgr)	IEC Strong (meq/dgr)	IEC Weak (meq/dgr)	$\%H_2O$	Film Thickness (mils)	Resistivity** (ρ^c) (ohm-cm)	Physical Condition of Film	Membrane ID
1	3.0	-NOT ANALYZED -			-	- -	-	many in matrix-severe leaks	CP2L3-60
2	2.0	-NOT ANALYZED -			-	- -	-	same as above	CP2L3-60
3	1.0	4.30	1.59	2.79	38	31	144	improved film - leaks in patches with bubbles	CP2L-56
4	0.5	3.00	1.64	1.36	36	27	154	homogenous leak-free areas predominate-leaks still present	CP2L-60
5	0.25	3.97	1.57	2.41	49	28	151	same as above	CP2L-64
6	0.12	NOT ANALYZED						under polymerized-tends to fragment and dissolve	CP2L2-64
7	0	NOT ANALYZED						same as above	CP2L2-64
8	1.0*	NOT ANALYZED						crosslinking appears low gelatinous weak resin	

* Diethyl benzene used as solvent

** Resistivity (ρ^c) measured at pH 4 with contact probes

Table 5: Physical and Chemical Properties of Vinylbenzyl Chloride-2-Vinylpyridine Copolymer

Test No.	Molar Ratio VBC/2VP	% Isobutanol	IEC Total (meq/dgr)	IEC Weak (meq/dgr)	IEC Strong (meq/dgr)	% H_2O	Film Thickness mils	Specific Resistance** ρ^c (Ω-cm)	Physical Condition of Film	Membrane ID No.
1	0.5	40	3.52	1.94	1.58	40	31	148	Severe leakage due to resin	CP2L-52
2	0.3	40	3.35	2.07	1.28	49	31	150	loss by adhesion to molds	CP3L-52
3	1.0	50	1.98	0.75	1.23	40	32	320	"	CP4L-52
4	1.5	40	1.86	0.92	0.94	34	27	365	"	CP14L-52
4A*	1.5	40	3.50	0	3.50	52	32	118	"	CP14L-T52
5	0.5	40	4.30	2.79	1.51	38	31	144	"	CP2L-56
6[1]	0.5	40	4.11	2.63	1.48	40	38	138	"	CP2AL-56
7	0.5	50	3.79	2.41	1.38	43	37	156	"	CP5L-56

Key: Mode of Mfg. Bulk Polymerization at 60-80° C, 17 hrs
Initiator - 1.0g AzoBisisobutyronitrile per 100 ml mixture
Support Fabric - 4 oz woven dynel #219

* Test 4A - sample of #4 aminated in trimethylamine
** Specific R (Ω) measured at pH 4 with contact probes
(1) monomers and solvent stirred together at 70° C for 1 hr.

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Table 6: Physical and Chemical Properties of Aminated PVC[1] Film as a Function of Time and Temperature of Reaction

	Aminating Conditions			Film Properties				
ID No.	Amine	Temp (^{o}C)	Time (hrs)	Thickness (mils)	Resistivity(ρ^{c}) at pH 4 (ohm-cm) [3]	IEC meq/dgr	% H_2O	Physical Condition
VCl-TP1	100% TEPA[2]	80	64	14	48	-	-	fragile
VCl-TP2	50% TEPA in isobutanol	80	64	10	72	-	-	fragmented
VCl-TP3	100% TEPA	25	16	7.0		-	-	unreacted
VCl-TP4	" "	50	16	7.0	405	1.7	29	strong,pinhole free
VCl-TP5	" "	50	42	8.7	270	3.2	45	" " "
VCl-TP6	" "	50	64	8.7	78	4.3	49	" " "
VCl-TP7	" "	50	17	8.0	340	1.5	23	" " "
VCl-TP8	" "	50	48	8.0	168[4]	2.75	42.5	" " "
VCl-TP8X	(post treated at 80^{o} C for 144 hrs in 2M $FeCl_3$,1M HCl)				160[4]	1.50	26.5	" " "

---

1. 8 mil polyvinyl chloride film, c-255 (Dayco Corp.)
2. TEPA - tetraethylene pentamine
3. Resistivity measured with platinized contact probes at pH = 4 at room temperature.
4. " " " " " " at 0.1 N HCl at room temperature.

Table 7: Physical and Chemical Properties of Solvent Cast Aminated PVC as a Function of Time and Temperature of Reaction

Membrane No.	Aminating Conditions		Film Properties		IEC	% H_2O	Physical Condition
	Temp (^oC)	Time (hrs)	Thickness (mils)	Resistivity ρ^c in pH 4 (ohm-cm)			
G1-27	25	64	12	>5000	<.03	62	strong-unreacted
G2-27	70	2	12	>5000	.33	75	" "
G3-27	70	4	25	>5000	.35	72	" "
G4-27	70	6.5	5.0	910	2.1	78	fragile, porous

Reaction Charge:

5 g	polyvinylchloride (GEON-Goodrich Chem.Co.)
40 ml	dimethylformamide (DMF)
50 ml	tetrahydrofuran (THF)
46 ml	tetraethylene pentamine (TEPA)

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Table 8: Properties of Polyethylene Film with Vinylbenzyl Chloride Graft

					MEMBRANE PROPERTIES					
Test No.	PE Film Pretreatment	Initiator (g/100 ml)	Film Contact Time (hrs)	Results	IEC (meq/dgr)	% H_2O	Thickness (mils)	Sp.Resist. ρ Ω-cm	Physical Condition	Membrane ID No.
1	Irradiated PE	0.15	2	good	2.1	32	28	92	stong,uniform	PV8-T49
2	Irradiated PE plus 2 hr VBC graft	0.15	2	good	3.4	47	47	28	mod.tear strength uniform	PV7-8T49
3	none	0.1	2,4,6	NG	High resistance, non-uniform film					PV3a-T44
4	none	0.5	<2	NG	Charge over polymerized - film not recovered					PV3b-44
5	none	1.0	<2	NG	Charge over polymerized - film not recovered					PV3c-44
6	swelled in toluene +1.0% BP, 70° C, 2.5 hrs	0	5	NG	High resistance non-uniform film					PV4-146
7	swelled in toluene 70° C - 1 hr	0.2	2	NG	High resistance non-uniform film					PV5-46
8	none; charge contained 10% toluene	0.2	2.5	NG	High resistance non-uniform film					PV5a-46

Key: PE film test 1,2: 20 mil LD tenite #1830 - 21 MEGARAD Irradiation, High Voltage Engineering Corp., Burlington, Mass.
test 3-8: 4, 10 mil low density polyethylene

Reaction- monomer charge - 800 ml VBC,4 ml 55% DVB
Conditions Initiator-Benzoyl peroxide
Temp.80-85° C
Post cure 1 hr at 70° C

Amination - 25% TMA - 17 hrs @ room temperature
Specific Res (ρ^c) measured with contact probes in 0.01 NaCl

Table 9: Effect of NP Solvent Fraction - Experimental Membrane Properties

Membrane	$f^{(1)}$ NP Solvent	% H_2O	IEC (meg/dgr)	R^c_ρ in 0.1 N HCl (ohm-cm^2)	P^+_{Fe} ($\frac{\text{mg Fe}}{\text{mF}}$)	E_{Fe} (3) (meq/mf)
A3L-18	.40	43.4	3.17	6.7	1.43	0.92
A3L-96	.35	39.8	3.12	9.4	0.066	0.996
C1L-93	.35	(42) (est)	(3.24) (est)	-	0.37	0.98
C1L-96	.30	37.6	3.24	6.4	0.071	0.996
CD1L-56	.40	46.8	4.29 (2)	-	0.22	.99
CD1L-96	.35	42.2	4.08 (2)	5.2	0.047	.997
103PZL	.42	44	2.1	7.8	43.0	1.2-2.3 (4)
103QZL	.38	36.7	2.3	9.5	1.0	0.95

Key: (1) Fraction of non-polymerizable solvent in monomer charge by volume

(2) CDIL, total strong and weak base IEC

(3) E_{Fe}, current efficiency based on meq Fe transferred per mF of electricity applied, (1-meq Fe/meq_{el})

(4) Transfer of Fe in 103 PZL greater than equiv. of electricity applied.

Table 10: Fe Permeation in Anion Membranes as a Function of Interstitial Molality, I_m

Membrane	IEC_T (meq/dgr)	% H_2O	I_M (meq/g H_2O)	P^{+}_{Fe} (mg Fe/mF)
103PZL	2.1	45.0	2.57	40
CD1L-Q 66	3.26	47.0	3.59	80
VC1-TPB	2.75	42.5	3.72	11.7
103QZL	2.3	36.7	3.90	1.0
A3L-18	3.17	43.3	4.15	1.43
VC1-TP8X	1.50	28.5	4.48	0.33
A4L-18	4.02	46.2	4.68	1.0
A3L-96	3.12	39.8	4.72	0.066
CD1L-56	4.29	46.8	4.88	0.22
C1L-96	3.24	37.6	5.37	0.071
CD1L-96	4.08	42.2	5.59	0.047
B2L-DT95	5.38	41.9	7.46	0.029

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Table 11: Resistivity Measurements by Two Methods: Liquid Junction and Contact Probes

		@ ambient temperature (~25° C				80°C	
Membrane	Thickness (mils)	R_ρ^C (Ω-cm^2)	ρ^C (Ω-cm)	R_ρ^J (Ω-cm^2)	ρ^J (Ω-cm)	R_ρ^J (Ω- cm^2)	ρ^J (Ω-cm)
103PZL	24	-	-	2.7	49.7	1.2	21.6
103QZ1	24	9.5	156	4.1	77.5	1.9	35.3
A3L-18	24	6.7	110	4.0	65.3	1.2	20.4
A4L-18	24	5.2	85	3.6	59.5	0.9	14.4
A3L-96	24	9.4	154	-	-	-	-
B2L-DT19[1]	27	-	-	6.6	95.6	1.8	25.8
B2L-DT95	27	8.0	116	-	-	-	-
B1L-DT19	26	-	-	5.9	89.5	1.7	26.2
B1L-D37	25	-	-	4.2	66.1	-	-
B2L-D37	27	-	-	4.7	68.6	-	-
C1L-B	20	-	-	2.3	45.9	0.9	17.0
C1L-96	27	6.4	93	-	-	-	-
CD1L-56	31	-	-	3.8	47.6	-	-
CD1L-96	27	4.9	71	-	-	-	-
CP2L-64	24	4.2	56	-	-	-	-
CE-1	29	5.7	76	-	-	-	-
VC1-TP4	7.0	-	-	1.9	106	-	-
VC1-TP5	8.7	-	-	0.9	41.8	-	-
VC1-TP6	8.7	-	-	0.9	42.5	-	-
VC1-TP8	8.7	3.7	175	-	-	-	-
VC1-TP8X	8.7	3.6	170	-	-	-	-
PV8-T49	28	-	-	3.5	28.9	-	-
PV7-8T49	47	-	-	0.7	10.2	-	-

Key:

R_ρ^C = area resistance by contact probe measurement in 0.1N HCl

ρ^C = resistivity by contact probe measurement in 0.1N HCl

R_ρ^J = area resistance by liquid junction measurement in 1.0N HCl

ρ^J = resistivity by liquid junction measurement in 1.0 N HCl

(1) = B2L-DT19 equivalent to B2L-DT95.

Table 12 : Resistivity Change in 2 M FeCl$_3$; 1 M HCl Solution at Room Temperature

Test Cell Concentration 2M FeCl$_3$, 1 M HCl/1 M HCl

Membrane ID No.	Initial Resistivity (ρ_o) ohm-cm	Final Resistivity (ρ_f) ohm-cm	ρ_f/ρ_o	% Change
VC1-TP4	93.5	122.3	1.31	+ 31
VC1-TP5	41.6	36.3	0.88	- 12
VC1-TP6	37.1	29.2	0.79	- 21
PV7-8T48	9.6	16.2	1.68	+ 68
A3L-18	53.2	117.4	2.21	+121
A4L-18	49.2	104.5	2.12	+112
B1L-D37	59.1	129.8	2.20	+120
B2L-D37	60.2	125.9	2.09	+109
B1L-DT19	76.3	118.6	1.56	+ 56
B2L-DT19	100.4	118.5	1.19	+ 19
C1L-B	31.1	58.5	1.90	+ 90
C1L-Q	27.3	42.2	1.54	+ 54
103PZL	32.8	66.5	2.03	+103
103QZL	68.5	218.8	3.18	+218
103PZL-DMA[1]	28.2	57.6	2.07	+107

1 - same basic structure as 103PZL but aminated with dimethylamine.

Table 13: Resistivity Change in FeCl$_3$ as Function of the Amino Group

Membrane ID No.	Functional Ionic Group	Amine Character No.	Amine Character Type	ρ_f/ρ_o	IEC (meq/dgr)	% H_2O	P^+_{Fe} (mgFe/mF)
B1L-DT 19	Benzyl diethlenetriamine	1 2	primary secondary	1.56	4.6	39.0	-
B2L-DT 19	Benzyl diethlenetriamine		"	1.19	4.9	39.0	(0.029)
VC1-TP4	Tetraethylenepentamine	1 4	primary secondary	1.31	1.7	29.0	.013
VC1-TP5	" "		"	.88	3.2	45.0	10.1
VC1-TP6	" "		"	.79	4.3	49.0	8.3
B1L-D37	Dimethylbenzylamine	1	tertiary	2.20	3.2	-	-
B2L-D37	" "		"	2.09	-	-	-
103PZL-DMA	" "		"	2.07	-	-	-
A3L-18	Pyridine	1	cyclic tertiary	2.21	3.2	43.3	1.43
A4L-18	"		" "	2.12	4.3	45.2	1.0
C1L-B	Dimethylethylamine	1	tertiary	1.90	2.7	44.0	
103QZL	Benzyltrimethylamine	1	quaternary	3.18	2.1	36.6	1.0
103PZL	" "		"	2.03	2.2	45.0	40.5
PV7-8T48	" "		"	1.68	3.4		

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Table 14: Permeation of Fe^{+3} in Various Experimental Anion Membranes

Membrane	Fe^{+3} Permeability, P_{Fe}^{+}, (mg Fe/mF) at sampling intervals Δ mF = 4.56					
	1	2	3	4	5	6
AR103QZL	.097	.209	.588	.846	.956	.963
AR103PZL	29.4	36.8	44.1	33.3	32.7	40.5
VC1-TP6	1.78	2.49	3.20	7.82	8.02	8.33
VC1-TP5	7.80	8.92	9.82	9.75	9.41	10.1
VC1-TP4	.007	.009	.010	.012	.013	–
PV8-T49	0.30	6.00	17.3	18.6	18.7	19.3
A4L-18	0.108	.437	.815	.995	.985	1.01

Key:

Current Density,CD= 60 ma/cm^2
Current, I = 0.367 amp
Flow rate = 90 ml/min = 1.5 cm/sec (linear velocity)
Test Solution= 2 M $FeCl_3$, 1M HCl
Mode of redox cell operation = charging polarity
(+ 1M HCl/2M $FeCl_3$,1M HCl-)

APPENDIX I

Analysis of Ion Exchange Capacity (IEC)

The IEC of the candidate resins prepared for the program was measured by methods commonly used in the industry and modified where needed to obtain reliable results. The resins contained a variety of strong and weak base amino groups. Frequently an individual resin possessed a mixture of different weak base amines and in several cases a mixture of both strong and weak base amine. As strong amines (quaternary) are ionized at all pH ranges and weak amines exhibit ionic activity over a wide pH range on the acid side, it was necessary to use two different analytic procedures for IEC determination.

(a) Strong Base IEC Procedure: The analysis involves the direct exchange of chloride and nitrate ions using a neutral or slightly alkaline medium for all exchange reaction steps

$$R^+Cl^- + \underset{\text{excess}}{NO_3^-} \longrightarrow R^+NO_3^- + \underset{\big\downarrow\ \text{analysis}}{Cl^-}$$

1. Convert die cut membrane sample (in duplicate) to the chloride form in 1N NaCl + 0.05 N NH_4OH solution with shaking for a minimum period of 1 hr. (The NH_4OH serves to convert any weak base amine salts to the non-ionized form of the amine.)

2. Wash sample with H_2O for 1 hr to remove the adsorbed salt and shake in a 100 ml aliquot of 1.0N $NaNO_3$ for a minimum of 1 hour.

3. Collect 100 ml aliquot of $NaNO_3$ and analyze for chloride by the Mohr method ($AgNO_3$ titrant with K_2CrO_4 indicator).

4. Repeat steps 2 and 3, add analyzed value for Cl^- to the first.

5. Recycle membrane sample back to chloride form, wash in H_2O and dry at 110° C for 1 hour.

6. Calculate IEC in terms of milliequivalents of exchanged Cl^- per gram of dry resin.

$$\text{IEC} = \frac{\text{exchanged chloride (meq)}}{\text{dry sample (gm) - weight of cloth backing (gm)}}$$

<u>(b) Weak Base IEC Procedure:</u> The weak base resin group included a variety of primary, secondary, and tertiary amines. In acid medium the weak amines are converted to the ionized amine salt form and behave as strong exchangers.

$$RNH_2 + H^+ \longrightarrow RNH_3^+$$

Unionized form Ionized form

Because of the wide range in the weak base amine ionization consta (pK_a), the resins exhibit a wide range of pH values at which they would be essentially completely in the ionized state. It was found that the A4L-18 membrane which has an aromatic cyclic tertiary amine (pyridinium HCl, pKa = 5.3) as the exchange group required a solution 0.1N in H^+ before a reproducible IEC could be obtained. This indicated that the external solution pH has to be several orders of magnitude higher than would be required for the free amine in solution. IEC vs acidity of the equilibrant solution is given below for the A4L-18 resin.

Equilibrant Solution Acidity	IEC (meg/dgr)
pH4	3.4
pH3	3.3
pH2	3.5
pH2 (24 hr standing)	3.0
0.1 N HCl	4.3
0.1 N HCl (24 hr standing)	4.3

To assure complete conversion to the ionized state and reproducible IEC values, the following procedure was used for the analysis of all the resins containing weak-base amino groups:

1. Convert die cut membrane sample (in duplicate) to the amine salt form in 1N HCl with shaking for a period of 1 hr.
2. Equilibrate the sample twice in two aliquots of 0.1 N HCl for total period of 1 hr.
3. Remove sample and wipe surface free of solution with soft tissue (this serves to minimize contamination of the exchange solution with stray droplets of 0.1 N HCl. Contamination by adsorbed HCl in the resin was estimated to be $<2\%$ of the measured IEC).
4. Place sample in 100 ml aliquot of 1 N $NaNO_3$ with shaking for a minimum of 1 hr.
5. Collect $NaNO_3$ aliquot and analyze for chloride using Mohr method.
6. Repeat steps 4 and 5 and add the analyzed value of Cl^- to first.
7. Convert sample back to the ionic form with 1N HCl, equilibrate in 0.1 N HCl, dry at 110^{o} C for 1 hr.
8. Calculate value for strong plus weak base IEC as described under section (a.6) above.

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9. In resin samples which possess both strong and weak base IEC, the above procedure yields the total IEC. In such a case, repeat the analysis with the same sample using the procedure for strong base IEC. Calculate the weak base IEC by difference.

$$IEC_{weak} = IEC_{total} - IEC_{strong}$$

APPENDIX II

Analysis of Membrane Water Content

The polymer matrix of the membrane becomes hydrophilic on acquiring ion exchange sites. The organic solvents used in the polymerization step are then replaced by water when the membrane is equilibrated in aqueous solutions.

The total imbibed water or water content of the resin is measured by the following procedure:

1. Convert die cut membrane sample (in duplicate) to leached chloride form in 1N NaCl followed by H_2O wash (or in 0.1N HCl in the case of weak base resin);
2. Remove sample, wipe free of surface solution, and weigh quickly in moist condition;
3. Dry sample at 110° C for 1 hr, re-weigh;
4. Calculate % H_2O on a wet resin basis.

$$\% \ H_2O = 100 \cdot \frac{\text{sample, wet weight} - \text{sample, dry weight}}{\text{sample, wet weight} - \text{backing weight}}$$

Note: possible error introduced by cloth variance $<$ 5%

APPENDIX III

Membrane Resistivity Measurement

The resistivity of the candidate membranes was measured by two different methods using:

(a) liquid junction conductivity cell;

(b) contact probes.

(a) Liquid Junction Measurement: The procedure involves measurement of resistance by means of a conductivity cell in which both surfaces of the test membrane are separated from the electrodes by an electrolyte. The membrane resistance is obtained by the difference between the cell resistance with and without the membrane in position. The cell configuration is:

electrode/electrolyte/membrane/electrolyte/electrode

The conductivity cell consists of two Lucite half cells with a circular cross-sectional area of 1.36 cm^2 and a depth of 2 mm which provide a liquid contact between the platinized (Pt black) platinum electrodes located at the rear of the cell cavity. Each half cell contains an inlet and exit channel to allow circulation of the electrolyte. Figs. A1, A.2.

The auxiliary apparatus consists of a 1000 Hertz impedance bridge (General Radio No. 1650B), chemical pump, solution reservoirs and constant temperature bath.

The resistivity measurements were made using 1N HCl as the electrolyte solution at ambient and 80° C temperature. The method of measurement is as follows:

A one inch diameter circle of membrane is clamped between the Lucite cell halves and the cell filled with solution. Five consecutive instrument readings, in ohms, are taken with the liquid flowing within the cell and averaged to give R_T, which represents the sum of the membrane resistance, R_M and the solution resistance, R_S.

$$R_T = R_M + R_S$$

Similarly, five readings, R_S , are taken of the cell containing the solution only.

The membrane resistance R_M is the difference:

$$R_M = R_T - R_S$$

Duplicate membrane samples are measured for each membrane type and converted to resistivity ρ^J .

$$\rho^J \text{ (ohm-cm)} = R_{M(avg)} \cdot \frac{1.36 \text{ cm}^2}{t_m}$$

1.36 cm^2 = cross-sectional area of cell

t_m = thickness of membrane tested in cm

The area resistance $R^J_\rho \text{ (ohm-cm}^2) = R_{M(avg)} \cdot 1.36 \text{ cm}^2$

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The precision of the measuring system estimated on the basis of 13 sets of R_s measurements at ambient temperature was found to be satisfactory for purposes of membrane ranking or screening.

The standard error for R_s was ± 0.015 ohms or about ± 1.0% for a 95% confidence level. Variations in cell geometry and temperature were possible sources of error but appeared to be quite negligible.

As the membrane resistance R_M was about 50% of the R_T value (or about equal to R_s), the magnitude of the error for individual R_M values was in the order of about ± 2%.

(b) Contact Probe Measurement: This method involves the direct measurement of membrane resistance by physical contact of two opposing probes on opposite side of the membrane sample. The probe method can only be used at ambient temperatures.

The apparatus consists of a small base mounted vertical thickness gage modified to hold two platinized resistance measuring probes. The probes have flat parallel contact surfaces 0.123 cm^2 in area and are coated with platinum black. The probes are connected to a 1000 Hertz impedance bridge (General Radio).

The resistance measurement is made by placing the membrane sample, pre-equilibrated in the designated electrolyte (0.1 N HCl), between the probes and applying finger pressure for a thickness gage measurement. Three readings are made of resistance and film thickness simultaneously and averaged.

The contact probe system is more rapid and convenient but less reproducible and precise than the liquid junction method. Differences in membrane resistance greater than 10% can usually be detected by the probe measurement. It was useful in the membrane stability testing program for monitoring relative changes in membrane resistance. It was also useful as corroborative data for the more sensitive analyses of IEC and Fe permeation.

A summary of the liquid junction and contact probe data at ambient and at room temperature is given in Table 11.

APPENDIX IV

Membrane Permeability Measurement

(a) Permeation Apparatus

The test unit consists of 5 lucite blocks 1/4" x 3-1/2" x 3-1/2" each containing a cavity or cell 1/2" in width and 2" in length each with an outlet and inlet tubing. The unit is assembled with membranes (with gasket) sandwiched between each cell. The end cells contain platinized titanium electrodes connected to a power source (Figs. A3, A4).

Cell IV represents the anodic redox half cell and contains a recirculating 2M $FeCl_3$, 1M HCl solution pumped from reservoir R. Cell III represents the cathode side of the redox half cell and is filled with a static solution of 1M HCl as the collecting medium for the Fe^{+3} permeate. Cell II is a back up collection cell. The contents of both cells are removed at suitable intervals for Fe analysis.

The solutions in Cells I and V are recirculated to flush out the gases and electrolysis products formed during the run.

The candidate anion membrane A_T is located between Cells III and IV. The membrane arrangement and flow system are designed to minimize loss of Fe permeant and stray contamination by the conc. $FeCl_3$ solution.

The auxiliary equipment consists of the following:

DC Power Supply 629 A + 00V - 0.75 A Hewlett-Packard

Vac. Tube Ammeter 412A Hewlett-Packard

Lab. Pump-Oscillating 7103-1 Cole Parmer
Constant Temp Baths - Precision Scientific Co.
Thermometers
Reservoir Flask - 1 liter

(b) Permeation Test Procedure

A solution of 2M $FeCl_3$, 1M HCl is recirculated at a flow rate of 90 ml/min (equivalent to cell linear velocity of 1.5 cm/sec). Cells II and III are filled with 1M HCl through bottom inlet. These compartments are open to atmosphere at the top outlet take to permit expansion by water transfer. When the electrode wash solutions are flowing a constant DC current of 367 ma is applied to the unit. At 20 min. intervals (equivalent to 4.56 mF) the current is stopped momentarily while the solution from Cells II and III are collected in 100 ml volumetric flasks and the cell refilled with fresh 1M HCl. The current is reapplied and the procedure repeated for a total of 5-6 times.

The Fe^{+3} is analyzed using the orthophenanthroline colorimetric method. Absorbancy readings are taken on a Bausch-Lomb Spectrophotometer.

The permeation factor P_{Fe} of the candidate membrane is expressed in mg Fe^{+3} transferred per millifaraday (mF) of electricity applied. The 5th and 6th collection intervals (60 to 100 min after start of test) appear to be reliable steady state points of reference for membrane evaluation.