

**MEMBRANE
AND
ULTRAFILTRATION
TECHNOLOGY**

Developments Since 1981

Edited by S. Torrey

**MEMBRANE
AND
ULTRAFILTRATION
TECHNOLOGY**

Developments Since 1981

Edited by S. Torrey

Copyright © 1984 by Noyes Data Corporation

No part of this book may be reproduced in any form
without permission in writing from the Publisher.

Library of Congress Catalog Card Number: 83-22009

ISBN: 0-8155-0977-4

ISSN: 0198-6880

Printed in the United States

Published in the United States of America by

Noyes Data Corporation

Mill Road, Park Ridge, New Jersey 07656

10987654321

Library of Congress Cataloging in Publication Data

Torrey, S.

Membrane and ultrafiltration technology.

Updated ed. of: **Membrane and ultrafiltration technology** / edited by Jeanette Scott. 1980.

Bibliography: p.

Includes index.

1. Membranes (Technology) -- Patents. 2. Separation (Technology) -- Patents. 3. Filters and filtration -- Patents. I. Scott, Jeanette. Membrane and ultrafiltration technology. II. Title.

TP159.M4T67 1984 660.2'84245 83-22009

ISBN 0-8155-0977-4

Foreword

The detailed, descriptive information in this book is based on U.S. patents, issued between January 1982 and June 1983 that deal with membrane and ultrafiltration technology.

The book contains two parts. Part I covers recent patent technology. Part II, an overview of membrane separation processes, provides a review of current technology and suggests possibilities for future research.

Part I is data-based material, providing information retrieved and made available from the U.S. patent literature. It thus serves a double purpose in that it supplies detailed technical information and can be used as a guide to the patent literature in this field. By selecting the significant information from the patents, the book presents an advanced commercially oriented review of recent developments in the field of membrane and ultrafiltration technology.

The U.S. patent literature is the largest and most comprehensive collection of technical information in the world. There is more practical, commercial, timely process information assembled here than is available from any other source. The technical information obtained from a patent is extremely reliable and comprehensive; sufficient information must be included to avoid rejection for "insufficient disclosure." These patents include practically all of those issued on the subject in the United States during the period under review; there has been no bias in the selection of patents for inclusion.

The patent literature covers a substantial amount of information not available in the journal literature. The patent literature is a prime source of basic commercially useful information. This information is overlooked by those who rely primarily on the periodical journal literature. It is realized that there is a lag between a patent application on a new process development and the granting of a patent, but it is felt that this may roughly parallel or even anticipate the lag in putting that development into commercial practice.

Many of these patents are being utilized commercially. Whether used or not, they offer opportunities for technological transfer. Also, a major purpose of this book is to describe the number of technical possibilities available, which may open up profitable areas of research and development. The information contained in this book will allow you to establish a sound background before launching into research in this field.

The information in Part II is from *Membrane Separation Technology in the 1980s*, prepared by H.K. Lonsdale of Bend Research, Inc. for the U.S. Department of Energy Jet Propulsion Laboratory, March 1982.

The table of contents is organized in such a way as to serve as a subject index. Other indexes by company, inventor and patent number help in providing easy access to the information contained in this book.

Advanced composition and production methods developed by Noyes Data are employed to bring these durably bound books to you in a minimum of time. Special techniques are used to close the gap between "manuscript" and "completed book." Industrial technology is progressing so rapidly that time-honored, conventional typesetting, binding and shipping methods are no longer suitable. We have bypassed the delays in the conventional book publishing cycle and provide the user with an effective and convenient means of reviewing up-to-date information in depth.

16 Reasons Why the U.S. Patent Office Literature Is Important to You

1. The U.S. patent literature is the largest and most comprehensive collection of technical information in the world. There is more practical commercial process information assembled here than is available from any other source. Most important technological advances are described in the patent literature.
2. The technical information obtained from the patent literature is extremely comprehensive; sufficient information must be included to avoid rejection for "insufficient disclosure."
3. The patent literature is a prime source of basic commercially utilizable information. This information is overlooked by those who rely primarily on the periodical journal literature.
4. An important feature of the patent literature is that it can serve to avoid duplication of research and development.
5. Patents, unlike periodical literature, are bound by definition to contain new information, data and ideas.
6. It can serve as a source of new ideas in a different but related field, and may be outside the patent protection offered the original invention.
7. Since claims are narrowly defined, much valuable information is included that may be outside the legal protection afforded by the claims.
8. Patents discuss the difficulties associated with previous research, development or production techniques, and offer a specific method of overcoming problems. This gives clues to current process information that has not been published in periodicals or books.
9. Can aid in process design by providing a selection of alternate techniques. A powerful research and engineering tool.
10. Obtain licenses—many U.S. chemical patents have not been developed commercially.
11. Patents provide an excellent starting point for the next investigator.
12. Frequently, innovations derived from research are first disclosed in the patent literature, prior to coverage in the periodical literature.
13. Patents offer a most valuable method of keeping abreast of latest technologies, serving an individual's own "current awareness" program.
14. Identifying potential new competitors.
15. It is a creative source of ideas for those with imagination.
16. Scrutiny of the patent literature has important profit-making potential.

Contents and Subject Index

INTRODUCTION	1
--------------------	---

PART I PATENT TECHNOLOGY

1. MULTIPURPOSE MEMBRANES	5
Polymeric Membranes	5
Mixture of Two Polyethers to Make an Ultrafiltration Membrane	5
Crosslinked Polyalkyleneimines	8
Hydrophilic Polyamide Membrane Filter Medium	10
Liquophilic Polyamide Membrane Filter Medium	13
Polyaryl Ether Sulfone Semipermeable Membranes	14
Blended Polymeric Membranes	17
Polyimide Membrane Having a Porous Layer	19
Crosslinked Polymer with Active Amino Groups	21
Composite Membranes	24
Having as a Base a Polymer Containing Amino Groups	24
Composite Isocyanurate Membrane for Reverse Osmosis	27
Microporous Substrate plus Layer of Polymer Containing Urazole Structures	30
Miscellaneous Membranes	33
Amino Acid Molecules Grafted onto Preformed Polymer Surfaces	33
Ultrathin Nonporous Membranes	35
Silicic Acid Heteropolycondensates	37
Membrane Configuration	39
Manufacture of Hollow Fiber Membranes	39
Highly Anisotropic Microporous Membranes	40
Arrangement of Hollow Fibers Having Selective Permeability	43

Hollow Fiber Cellulose Acetate	45
2. ELECTROLYSIS OF BRINE	47
Diaphragms for Chlor-Alkali Cells	47
Electrolyte-Permeable Sepiolite Diaphragm	47
Process for Producing a Porous Polytetrafluoroethylene Diaphragm	49
Fluorinated Resin Diaphragm with Strong Hydrophilic Character	54
Permionic Membranes for Chlor-Alkali Cells	56
Permionic Membrane Hydrolyzed <i>in Situ</i>	56
Membrane with Different Cation Exchange Group Concentrations on its Two Sides	58
Dialkyl Perfluoro- ω -Fluoroformyl Diesters	61
Composite Fluorinated Membrane Containing Ion Exchange Groups	62
Copolymer of a Fluorinated Olefin and a Fluorovinyl Compound	65
Fabric-Reinforced Membrane	67
Surface Modification	70
Anode and/or Cathode Surfaces Characterized by Microporous Channels	72
Fluorocarbon Polymers with Pendant Carboxylic and Sulfonic Acid Groups	74
Fluorinated Polymer with Hydration Product Less Than 22,000	85
Fluoropolymers Treated with Amines	87
Method of Preparing a Permionic Membrane	89
Layered Fluorinated Copolymer	92
Permionic Membrane Cell with Hydrophilic Resin Between Electrocatalyst and Membrane	93
Designs for Chlor-Alkali Cells	95
Cylindrical Cation Exchange Membranes for Use in Finger Type Electrolytic Cells	95
Cathode Box Having a Number of Pocket-Type Cathodes	99
Vertical Cathode Pocket Assembly for Membrane-Type Cells	100
Construction and Operation of Chlor-Alkali Cells	102
Cell-to-Cell Catholyte Series Flow	102
Method of Bonding Cation Exchange Membranes	104
Bonding a Permeable Metal Layer to a Permionic Membrane	106
Two Separable Membrane Layers	108
Having One or Both Electrodes Held Against the Membrane by a Composite Layer	110
Solid Polymer Electrolyte Chlor-Alkali Cells	112
Intercalation Carbon-Fluorine Cathode Catalyst	112
Miscellaneous Processes	116
Measuring Cation and Water Transport Numbers	116
Regeneration of Permselective Ion-Exchange Membranes	117

3. OTHER ELECTROLYTIC PROCESSES AND APPARATUS.	120
Electrodialysis Processes.	120
Electrical Energy from Acid-Base Neutralization in Bipolar Membrane Cells.	120
Process for Regenerating Copper Plating Solutions.	122
Using Layered Anion-Permeable Membrane	124
Ion Transfer Membrane Assembly.	126
Using a High-Performance Bipolar Membrane	128
Ion Exchange Membranes for Various Uses.	131
Quaternization Process for Hollow Fiber Membranes	131
Subjecting Membranes to a Gas Plasma Treatment.	134
Cation Exchange Membrane Reinforced with Woven, Bulked Fabric	135
Production of Membranes with Low Electrical Resistance.	138
Battery Separators.	140
Sealing Glasses for Membranes in Sodium-Sulfur Batteries.	140
Microporous Polyolefin Film with Inorganic Filler.	142
Hydrophilic Polymer-Coated Microporous Membranes	145
Preparation of β - or β'' -Aluminas for Half-Cell Separators in Sodium-Sulfur Batteries	146
Membrane with Increased Ion Selectivity.	147
Solid Polymer Electrolyte Cell Separators	149
Graft Polymer.	151
Miscellaneous Processes and Related Apparatus.	154
Electrically Augmented Vacuum Filters:	154
Regeneration of Spent Chromium Solutions.	156
Fuel Cell with Metal/Acid Ion Permeable Membrane as Fluid Barrier.	158
Assembly of Electrolytic Membrane Cell	162
4. SEPARATION PROCESSES FOR GASES, LIQUIDS AND DISSOLVED SOLIDS.	166
Gas Separations.	166
Separation of a Selected Gas Through an Ion-Exchange Membrane	166
Hydrogen Diffusion Through Inorganic Anisotropic Hollow Fibers	168
Separation of Low Molecular Weight Gases.	171
Ultrafiltration Systems.	174
Use of a Semipermeable Membrane to Concentrate Uranium from a Solution	174
For Anthocyanin Pigment Extracts.	177
Preparation of Radiation-Sensitive Silver Halide Dispersions	180
Method for Producing Solute-Rejecting Dynamic Membrane Filters	182
Tubular Membrane Apparatus Easily Disassembled for Cleaning.	184
Preparation of Vinyl Resin Latices by Emulsion Polymerization.	186
Ultrafiltration and Reverse Osmosis Device.	188

Recovery of Solvent from a Foots Oil Solution	190
For Separation of Inosine and Guanosine from Fermentation Broth	193
Porous Vinylidene Fluoride Membranes	194
Pressure Filtration	196
Preparation of Concentrated Stable Dyestuff Dispersions	196
Using a Linear Polyurethane Ultrafilter	198
Ion Exchange Methods	200
Regeneration of Waste Photographic Processing Solutions	200
Removal of Sodium and/or Potassium Ions from Glass Polishing Bath	202
Hollow Fiber Permeators for Fluid Separations	203
Method for Inserting Hollow Fiber Membranes Into Permeator Shell	203
Producing Enhanced Performance by Longitudinally Compacting the Fibers	205
Tube Sheets Prepared from Polyglycidyl Resin and Filler	207
Tube Sheets Prepared from Polyglycidyl Resin and Imidazole Curing Agent	211
For Specialized Separations	212
Removal of Organics from Aqueous Solutions	212
Separation of Multivalent Metal Ions from Aqueous Solutions by Microcapsules	213
Separation of Multivalent Metal Ions from Aqueous Solutions by Emulsion	215
Safe Recovery of Inflammable Solvents	216
Separation of Organic Liquid Mixtures	219
Separation of Anions and Cations from Aqueous Solution by Liquid Membranes	221
Leak-Tight Mounting of Membranes to a Support Plate	223
5. HEMODIALYSIS	225
Dialysis Systems and Associated Components	225
Kilil-Type Artificial Kidney	225
Dialyzer Producing a Rapid, Toroidal-Patterned Dialysate Flow	228
Dialyzer Having a Thin Wall Plate	229
Drainage System to Prevent Spillage	232
Flow Reversal System for a Negative-Pressure Dialyzer	233
Dialyzer in Which Blood and Dialysate Are Mixed Within Conduits	234
Ultrafiltration Control Device	237
Automated Diaphragm Single Pass Dialysis Apparatus	240
Hollow Fiber Dialyzers and Their Components	242
Potting the End of a Bundle of Hollow Fibers Positioned in a Casing	242
Manufacture of Hollow Fiber Fractionating Cells	244
Diffusion Membrane Units with Adhered Semipermeable Capillaries	247

Capillary Fiber Bundles	250
Portable Dialyzers and Their Components	251
Artificial Kidney with Separable Parts	251
Stack Assembly Composed of Two Kinds of Cells	253
Membrane Separation Cell.	255
Dialysis Membranes	256
Polyether-Polycarbonate Membranes.	256
Ethylene-Vinyl Alcohol Copolymer	258
Hollow Fiber Membranes of High Molecular Weight	260
Noncytotoxic Polyurethane Membranes.	261
Viscose Membranes	263
Miscellaneous Dialysis Procedures	266
Regulation of Hemodialysis to Prevent Hypotension	266
Sodium Bicarbonate Dialysate Prepared in Plural Stages	268
Automated Cleaning System for Dialyzers	271
Apparatus for Preventing Air from Entering an Artificial Kidney	273
6. OTHER MEDICAL APPLICATIONS	276
Blood Oxygenators	276
Catalytic Membranes Used in Artificial Lungs	276
Silicone Rubber Gas-Exchange Sheet Member.	279
Transfer Membrane Assembly	281
Hydrophobic Diffusion Membranes Having a Hydrophilic Outer Surface	283
Catalytic Membranes for Artificial Organs	286
Peritoneal Dialysis	287
Filter Arrangement to Deny Bacteria Entry to Peritoneum	287
System for Use in the Home	290
Blood Fractionation Processes	292
Membrane Plasmapheresis Module	292
Fractionation of Blood Plasma Proteins	294
Removal of Gamma Globulin Aggregate from Gamma Globulin	297
Apparatus Using Alternate Opposite Flow Directions Across a Membrane	298
Separation of Serum Albumin and Gamma Globulin	300
Apparatus for Obtaining a Desired Rate of Plasma Flow	302
Blood Purification	303
Using Hollow Fiber Type Membranes	303
Apparatus Using Plural Ultrafiltration Steps	306
Immobilization of Biologically Active Materials on a Semipermeable Membrane	309
Analysis of Biological Liquids	313
Measurement of Potassium Ion Content of Biological Liquids	313
One-Piece Disposable Electrode	315
Drug Delivery Systems	317
Osmotic System for Controlled Release	317
Lipid Membrane Structures for Carrying Drugs to Liver	320
Microencapsulation	323

Of Labile Biological Materials	323
Of Tissues or Individual Cells	325
Artificial Red Cells	328
Miscellaneous Procedures and Products	330
Provision of Continuous pH Control for Stored Blood	330
Artificial Endocrine Pancreas	332
Nonthrombogenic Materials of Polymer Bonded to Heparin	334
Extracorporeal Hemodialysis as Treatment for Sickle Cell Anemia	336
Preparation of Immunologically Active Aggregates of Amphiphilic Membrane Proteins	339
Multipurpose Multichanneled Diffusion Device	342
7. WATER PURIFICATION	345
Desalination	345
High Temperature Electrodialysis	345
Composite Lyophobic-Lyophilic Membrane	348
Apparatus with High Reliability Requiring Minimum Upkeep	349
Desalination Apparatus Having No Moving Parts	350
Permselective Membrane of Crosslinked Methylolated Vinyl-Phenol Polymer	353
Semipermeable Asymmetric Cellulose Acetate Membrane	355
Systems for "Point of Use" Areas	357
Composite Semipermeable Membrane	360
Reverse Osmosis Membranes and Systems	362
RO Membrane Having Simple Method for Cleaning Outer Permeate Channel	362
RO System Having Means for Creating a Pressure Differential Across the Membrane	365
Ultrathin Membrane Crosslinked on the Surface by Exposure to a Plasma	368
Rotating Solution Separation System	370
Sterile and Bacteria-Free Water	372
Distillation Systems Including Reverse Osmosis Units	374
Thin High Polymer Film Attached to a Porous Base	376
Utilizing Plural Flow Work Exchangers	379
Apparatus Without a Mechanical Reciprocating Drive System	381
RO Membrane Casting Solution	383
Composite Membrane Having Controlled Thickness	384
Miscellaneous Processes	387
Increasing Cross-Flow Microfiltration Fluxes of Wastewaters	387
System for Water Recovery from Waste Liquids for Use in Space Flights	389
Production of Soft Water with Low Total Dissolved Solids	392
Water Treatment System in Which Treated Water May Be Stored Under Pressure	395
Apparatus for Cleaning Membrane Filtration Units	396

8. MISCELLANEOUS USES FOR MEMBRANES	399
Roofing Membranes	399
Sealing Membrane with Incorporated Limited-Slip Sheet.	399
Weatherproof High Strength Triaxial Membrane for Radome Cover	401
Dimensionally Stable PVC Membrane	403
Durable Flexible Membrane	405
Other Products	407
Fiber-Reinforced Membrane for Asphalt Paving.	407
Oil-Filter Sealing Membrane	410
Water-Permeable Hydrophobic Membrane for Outer Layer of Disposable Diaper	412
Water-Permeable Grasslike Sport Surface	414
System to Cause Circulation of a Solution	416
By Use of an Asymmetric Microporous Membrane.	416

PART II OVERVIEW

1. INTRODUCTION AND SUMMARY	421
2. STATE OF THE ART OF MEMBRANE SEPARATIONS	423
Technology	424
Membranes	424
Modules	425
Equipment Design	429
Applications	431
Science	433
3. CURRENT ACTIVITIES IN MEMBRANE TECHNOLOGY	437
Conventional Approaches	437
Unconventional Approaches	438
Thin Membranes	438
Improved Permselectivity	439
Alternative Engineering Approaches	441
Nonseparation Applications	444
Biotechnology	444
Energy from Sunlight	445
4. FUTURE DIRECTIONS	446
Where to Look	447
How to Look	448
5. REFERENCES	451
COMPANY INDEX	455
INVENTOR INDEX	457
U.S. PATENT NUMBER INDEX	461

Introduction

This book on membrane technology may be viewed as a study of the latest techniques for the separation and purification of fluids. The book contains two parts. Part I describes recent patent technology in the field, and Part II is an overview of membrane separation processes which provides a review of current technology and suggests some possibilities for future research.

A membrane is defined as a thin sheet of natural or synthetic material which is permeable to substances in solution. A semipermeable membrane, the use of which is delineated in this book, is a natural or synthetic microporous structure which acts as an efficient filter for particles in the range of molecular dimensions.

In 1861 Thomas Graham, a British chemist, first observed the marked difference in the rates of the diffusion of certain substances through a parchment membrane. His studies led to the development of colloid chemistry. The rates of diffusion of various sized molecules vary widely; e.g., the diffusion rate of sodium chloride is 2.3, that for sucrose is 7 and for such macromolecules as proteins the rate is from 50 to 100. These diffusion rate differences establish the separation and purification processes of this book.

There are three types of barrier separation processes—filtration, with which we are not concerned here, ultrafiltration, and osmosis. Filtration applies to particles greater than approximately one micron in diameter. Ultrafiltration is the process in which colloidal particles or large molecules (generally greater than about 20 Angstrom units in diameter) are separated from solution. The process of osmosis is potentially capable of separating low molecular weight salts from their solvent.

Part I is divided into eight chapters. In the first chapter, semipermeable membranes which are useful for more than one kind of procedure are described; e.g., membranes which can be used for dialysis and for desalination.

Chapter two involves the electrolysis of brine to chlorine and sodium hydroxide in cells of the diaphragm or permionic type. This procedure is of great importance industrially.

The third chapter takes a look at other electrolytic processes involving membranes—electrodialysis (a process in which dialysis is accelerated by the use of an electric field), membranes used as battery separators, etc.

Chapter four examines the various kinds of membrane separation processes for fluids which are not specifically covered in other chapters, and apparatus designed for such separations.

The fifth and sixth chapters have to do with medical applications of membrane techniques. The whole of chapter five deals with the blood-washing technique based on dialysis in which the dialyzer and the machine which operates it act as an artificial kidney. Hemodialysis removes the toxic metabolites usually contained in urine from blood of patients who are suffering from chronic kidney disease. Hemodialysis was first used on humans in 1945 and the development of hollow filaments of cellulosic or synthetic polymers made possible the introduction of more compact dialyzers in the late 1960s. New types of membranes and new dialyzer designs to make dialysis faster, less expensive and safer for the patient continue to be invented.

Chapter six looks at other medical applications for semipermeable membranes. These include artificial lungs or blood oxygenators, processes for the fractionation of blood, and drug delivery systems, for example.

The seventh chapter deals with the subject of water purification, and includes various desalination processes and means of wastewater purification. This subject becomes more important each year, as the world's supply of pure water dwindles inexorably.

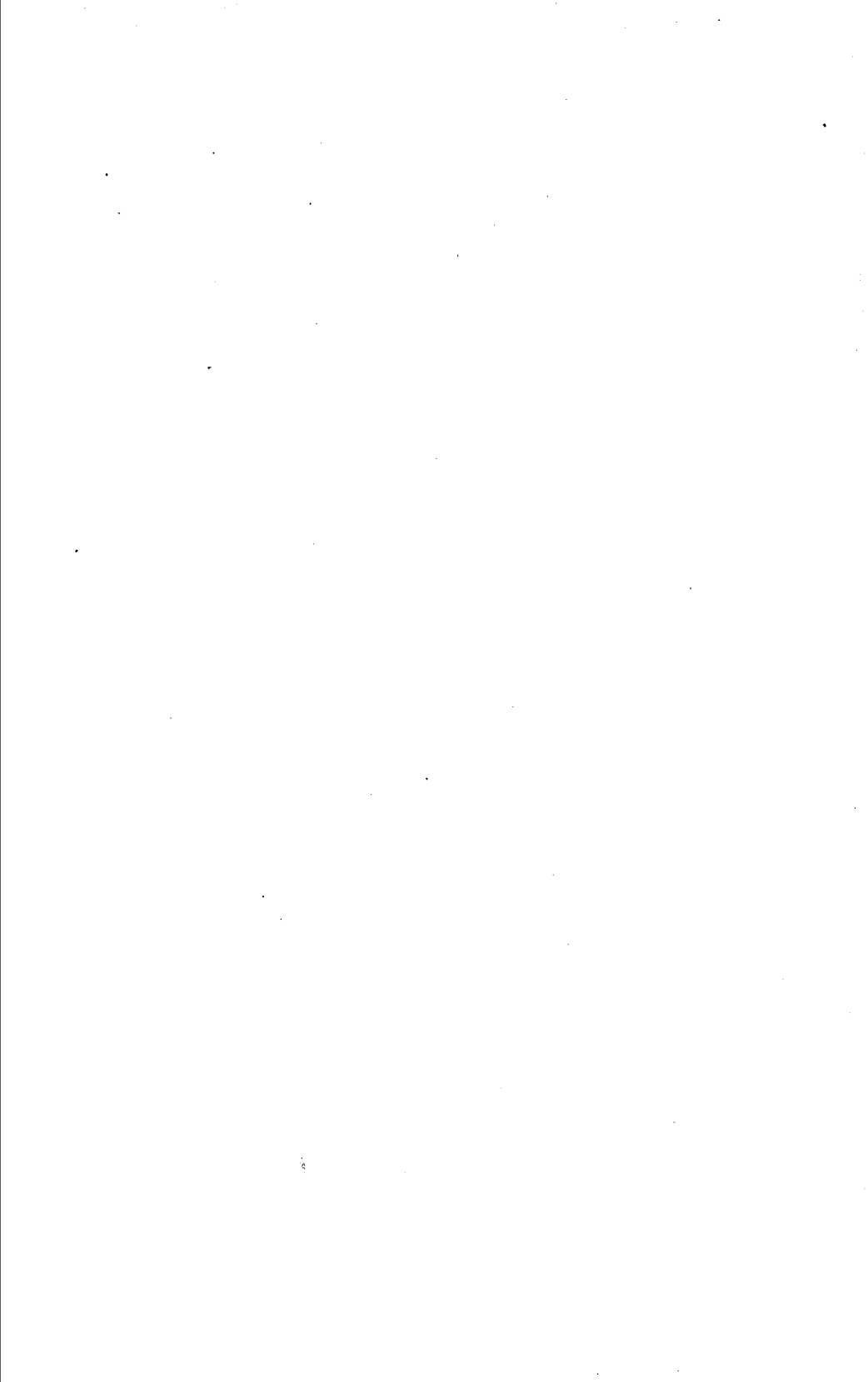
Chapter eight covers miscellaneous uses of membranes—for roofing, road paving, artificial sports surfaces, etc.

It was, of course, difficult to assign these patents to one particular chapter. Definitions of terms used in membrane technology show how much overlapping there is in the concepts—dialysis and ultrafiltration, for example, seem nearly indistinguishable—and many of the patents could well have been placed in another location in the book. It is felt, however, that a perusal of the headings listed in the Contents and Subject Index will enable persons interested in specific types of processes to find the patents which are applicable.

Part II, as noted above, presents an overview of the state of the art of membrane separations—the technology, applications, and science. Current activities and future directions are also covered.

Part I

Patent Technology



Multipurpose Membranes

POLYMERIC MEMBRANES

Mixture of Two Polyethers to Make an Ultrafiltration Membrane

X. Marze and M. Minfray; U.S. Patent 4,319,008; March 9, 1982; assigned to Rhone-Poulenc Industries, France.

It is well-known to this art to utilize semi-permeable membranes in various separation processes, such as reverse osmosis and ultrafiltration.

For such applications, it is advantageous to fabricate screen-based or reinforced membranes, namely, membranes which comprise, for at least a portion of their thickness, a flexible support or backing [which is frequently a fabric, non-woven or grid], which support renders the membranes both strong and easy to handle, even when in the form of samples having large dimensions. Screen-based membranes are generally produced by casting a polymer solution, followed by removal of the solvent [notably by evaporation and/or coagulation]. The polymer solution is hereafter referred to as the "collodion", regardless of the polymer envisaged.

Thus, the present invention features novel semi-permeable membranes which can be widely used in industry, in particular for purposes of ultrafiltration, and which are based on a polymeric composition of polysulfone type but which can be fabricated from fairly concentrated collodions.

The membranes according to the invention are characterized in that they comprise a mixture including at least one polymer (polyether) comprising recurring units of the structural formula (I):