MEMBRANE TECHNOLOGY AND INDUSTRIAL SEPARATION TECHNIQUES

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FOREWORD

The detailed, descriptive information in this book is based on U.S. patents issued since 1960 and relating to the technology of membranes and industrial separation techniques. Included also are one published patent application and one reissue of a patent published earlier.

This book serves a double purpose in that it supplies detailed technical information and can be used as a guide to the U.S. patent literature in this field. By indicating all the information that is significant, and eliminating legal jargon and juristic phraseology, this book presents an advanced, technically oriented review of membrane technology and industrial separation techniques.

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 to research and development. The information contained in this book will allow you to establish a sound background before launching into research in the field.

Advanced composition and production methods developed by Noyes Data are employed to bring our new 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.

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.

15 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.

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. Copies of U.S. patents are easily obtained from the U.S. Patent Office at 50¢ a copy.

15. It is a creative source of ideas for those with imagination.

CONTENTS AND SUBJECT INDEX

INTRODUCTION

Semipermeable membranes have recently gained commercial importance as a result of their employment in the treatment of aqueous solutions in order that water having greatly reduced amounts of impurities is caused to flow through the semipermeable membrane. These treatments are carried out using high pressure, above the osmotic pressure of the solution being treated, which causes water flux through the membrane to occur, and has been commonly referred to by the term "reverse osmosis."

Semipermeable membranes are now being used in the reverse osmosis treatment of aqueous solutions either for production of relatively pure water or for concentration of the solution being treated or both. Such semipermeable membranes have been produced from various polymeric materials, such as esters of cellulose. More recently, semipermeable membranes of this type have been fabricated from polyamides, polyimides, polyphenyl esters, polysulfonamides, polybenzimidazoles, polyarlyene oxides, polyvinyl methyl ether, and other polymeric organic materials.

In general, cellulose derivatives, such as cellulose acetate, cellulose acetate butyrate, cellulose propionate, ethylcellulose and other cellulose esters and mixed esters, have found ready use in fabricating so-called asymmetric membranes where the semipermeability of the membrane results from a thin, dense skin located at one surface of the membrane, with the remaining major part of the membrane providing a more porous supporting layer formed of the same polymer.

Somewhat more recently, a great deal of work has been done in developing what are now known as "composite" membranes, where semipermeability results from an ultrathin polymeric film of one material which is formed separately and is supported on an underlying porous substrate that may be made from a different polymer than the ultrathin film.

Membranes for carrying out hyperfiltrations have very diversified applications, including for instance:

(1) The recovery of water from saline solutions, e.g.,

the desalination of seawater;
the demineralization of fresh water;
the purification of industrial effluents; and
the purification of rivers and waterways.

(2) The recovery of small quantities of dissolved or colloidally dispersed sub-

stances from solutions containing the same, e.g.,

the recovery of metals from industrial effluents; and
the concentration of hormones, vitamins, inoculants and vaccines, etc.

(3) The concentrations of solutions or dispersions of available products that are thermally and/or chemically unstable or fugitive, e.g.,

the concentration of fruit and vegetable juices;
the concentration of sugar solutions;
the preparation of beverage extracts (milk, coffee, tea, etc.); and
the concentration of sera.

(4) The separation and purification of macromolecular or colloidal substances from solutions containing low molecular weight impurities, e.g.,

the purification of blood;
the use in artificial kidney machines; and
the separation of alkaloids, amino acids, glycosides, etc.

This book presents over 280 processes as described in the U.S. patent literature during the past fifteen years. Overall, hundreds of formulations, casting procedures, fabrication techniques and end use applications are described for every major industrial phase of membrane technology.

The first four chapters are devoted to the preparation of membranes, separators and modular units employing cellulosics and a wide variety of other polymeric materials. While largely described for use in desalination processes by reverse osmosis, it is obvious that many of these systems will find broad commercial utility as this rapidly growing area of technology matures over the next decade.

Ion exchange membranes are described in the fifth chapter and some specific industrial membrane separation processes relating to gas and liquid separation, catalyst and heavy metal removal and a very active area, hemodialysis and other medical applications, are described in the final three chapters.

CELLULOSIC MEMBRANES–REVERSE OSMOSIS

SOLVENTS AND ADDITIVES FOR CASTING BATHS

Basic Process

A process described by *S. Loeb and S. Sourirajan; U.S. Patent 3,133,132; May 12, 1964; assigned to The Regents of the University of California* is directed to a porous membrane capable of desalinizing brine solutions at much higher flow rates of the desalinized water than has been found possible by use of porous membranes previously known. The membranes of this process have been found capable of reducing the concentration of a 5.25% sodium chloride solution to 500 parts per million in a single pass at a flow rate on the order of 8 gallons per square feet of membrane surface per 24-hour day under a pressure differential of 1,500 psig, the membranes having been approximately 1½" and 4¼" in diameter, respectively, and approximately 0.004" in thickness. The membranes receive a permanent set or strain such that their final thickness may be 0.0025".

The process involves the preparation of a film-casting solution from which a film is cast and then treated and prepared as described. To provide an understanding generally of the method of preparing the films or membranes, it may be pointed out at the outset that the film-casting solution from which the films are cast contains a pore-producing agent (i.e., this agent produces a structure which allows appreciable rate of passage of fresh water under suitable condition) of the nature of aqueous perchlorate salt solution in a suitable ratio to a film material such as cellulose acetate.

Magnesium perchlorate is preferred but other inorganic perchlorate salts may be utilized, such as sodium perchlorate salts. A solvent, preferably acetone, is added to prevent the solution from becoming too viscous. Methyl ethyl ketone, ethyl alcohol and/or methyl alcohol may also be used but not as efficaciously, as the solvent or solvents. The film material may also be other cellulosic esters and cellulosic derivatives.

Next, film casting and subsequent solvent evaporation into air is accomplished most conveniently and efficiently, but not essentially, at reduced temperatures to reduce the solvent evaporation rate and permit effective initiation of the desired organization of the water-cellulose acetate structure; then, after a predetermined time such that the solvent is not completely evaporated, the film is immersed in water, preferentially but not essentially ice water, to prevent complete air-drying of the film. Complete air-drying has been found to be harmful in that it reduces the desalinizing capacity of the film and is believed to damage the water-cellulose acetate structure which has been initiated.

Finally, the film is preferably heated prior to use to complete the organization of the film for high-flow desalinization of seawater. For certain applications, where the ions to be separated are large relative to those predominant in seawater it would not be necessary to heat the film. The following is a detailed description of a specific preferred example of the formation of the solution and casting, treatment, and preparation of the film in accordance with this process. A solution is prepared containing components as follows.

(A) Aqueous magnesium perchlorate. The concentration of magnesium perchlorate in this aqueous solution may be varied from 5% by weight up to saturation concentration, approximately 50% by weight of $Mg(ClO_4)_2$. The 10% concentration is preferred. As the aqueous concentration of magnesium perchlorate is increased above this figure, the flow rate of the water through the completely treated membrane is progressively reduced. If the water is omitted completely from the casting solution, the flow rate from the subsequently made film is very low, and, in the two tests made, did not appear to be influenced by the amount of magnesium perchlorate present. At aqueous concentrations below 10%, there is inadequate magnesium perchlorate to maintain the desired relation between water and cellulose acetate such that in the film the desired organization can be obtained. The aqueous magnesium perchlorate solution is referred to as MP.

(B) Cellulose acetate containing preferably 54 to 56% by weight of combined acetic acid (CA).

(C) Acetone (A).

The proportions of these materials in the foregoing solution is subject to some variation. However, the region wherein the best results are obtainable is found to be that where the ratio of A to CA is to be between 2:1 and 4:1 by weight; and the ratio of MP to CA is to be between 1:1 and 1:3 by weight. A preferred and representative solution is MP, 11%; CA, 22% and A, 67%. Another representative solution is a mixture of cellulose acetate, acetone, water and magnesium perchlorates in the percentages 22.2, 66.7, 10.0 and 1.1%, respectively. An example of the process follows.

Example: The casting was done on glass plates with runners on the sides, of a thickness, i.e., height, above an associated glass plate to maintain the desired thickness of casting. Preferred runner thicknesses are approximately 0.010" for a film of approximately corresponding thickness. Both solution and the plates on which the film was cast were cooled in a cold box to a temperature of approximately -7.5° to -16°C. The film was cast by means of a doctor blade or knife which rested on the raised runners at the edges of the glass plate. The doctor blade guided the film on, and by the suitably spaced runners, was pulled across the plate in predetermined spaced relationship thereto at a rate such that the entire width of the plate, which was 8" (representatively) was accomplished in 0.17 minute although this time range has been varied from 0.13 to 0.25 minute without adversely affecting the results.

Too slow a period of time permits excessive evaporation. Too fast a sweep time results in imperfect surface formation or even rupture of the film. The doctor knife also served as the back wall of an open-bottomed box, ½" high, filled with 40 cc of casting solution, prior to casting. During casting, 35% of the solution was spread on the plate, leaving enough solution in the box so that the static head available for flow under the knife did not decrease excessively as the knife was pulled from one end of the plate to the other.

After casting the film on the plate, solvent evaporation was allowed to proceed in a cold box at -7.5° to -16°C (optimum -11°C). It was allowed to remain in the cold box at the same temperature for a period of from 2 to 4 minutes to permit evaporation of a major portion of solvent and initial organization of the film after which it was immersed in water at approximately 1° to 5°C. This completed removal of the solvent and probably some of the magnesium perchlorate by diffusion into the water. The time of 2 to 4 minutes between casting and immersion was critical. Too short a time prevented the formation of a firm film. Too long a time prevented the film from having good desalinization qualities.

Therefore, it is clear that the primary function of the immersion is not to extract the materials, but to obtain the film structure necessary for optimum results. The optimum time appeared to be 3 minutes. The optimum permeability structure in the finished membrane apparently need not necessarily be the same for all desalinizing membranes; it can vary depending upon the chemical nature of the membrane and the saline water solution. The thickness of the finished films is not critical in view of the apparent surface nature of the barrier effect. A film of membrane of the order of 0.004" is appropriate.

A preferred technique for heating the films consists in setting them or placing them under water on glass plates which are separated by washers, as of brass, $\frac{1}{32}$" thick, that is, with one on top of another. The brass washers merely keep the top glass from bearing directly on the film. The assembly is then heated up on a hot plate. The film after heating in the water bath is left there for a period of time before being taken out to use. The water bath is between 77° and 83°C and the optimum temperature is 82°C. It is preferable to heat the water up to the desired temperature for one-half hour gradually. The water may be put in at 50°C and then heated up to 82°C and held for at least approximately an hour but can be left overnight or longer and then allowed to cool.

The foregoing results in what may be described as an opalescent film in that it is transparent but has a certain characteristic opalescent appearance. It has a porosity, i.e., ratio of open volume to total volume, in the order of 25 to 40%. A significant aspect of the film is that one side is useful whereas the other side is not. The side which is away from the glass plate during casting is the side which must be used against the salt solution. The other side is assembled against a porous plate.

Tests have been carried out in both a laboratory-scale and a bench-scale test cell providing: (1) a constant high pressure on the saline water in contact with one side of the porous medium; (2) a continuous source of flowing or turbulent food saline water to the high pressure side of the porous medium; (3) a valve for the continuous or intermittent removal of concentrated solution to prevent the accumulation of salt concentration in the cell; and (4) a means of exit for the demineralized water to the outside of the cell at atmospheric pressure.

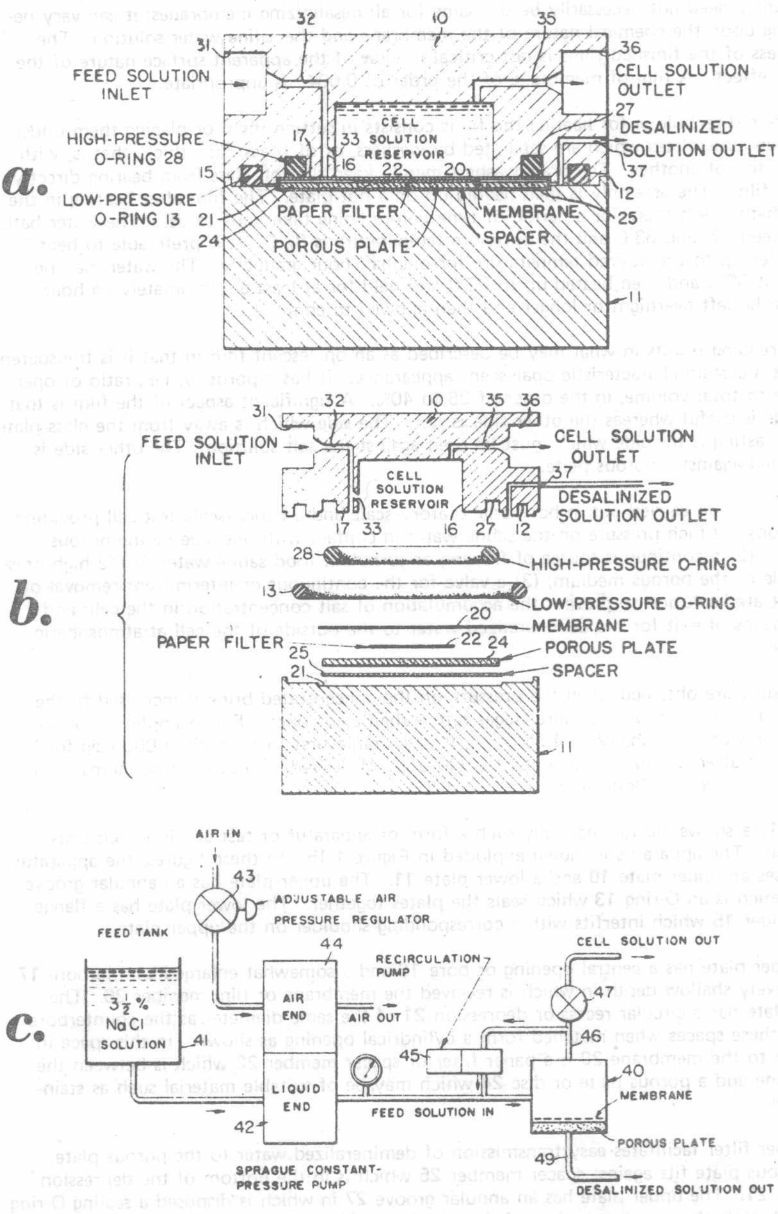
Best results are obtained when the pressure on the concentrated brine is increased to the operating pressure in one or more stages rather than all at once. For example, if the operating pressure will finally be 1,500 psig, it is desirable first to maintain 1,000 psig for ½ hour; then after ½ hour, increase it to 1,500 psig. If desired, it may then be increased to 2,000 psig, at least 1 hour later.

Figure 1.1a shows diagrammatically such a form of apparatus or test cell in which tests were run. The apparatus is shown exploded in Figure 1.1b. In these figures, the apparatus comprises an upper plate **10** and a lower plate **11**. The upper plate has an annular groove **12** in which is an O-ring **13** which seals the plates together. The lower plate has a flange or shoulder **15** which interfits with a corresponding shoulder on the upper plate.

The upper plate has a central opening or bore **16** and a somewhat enlarged counterbore **17** of relatively shallow depth in which is received the membrane or film member **20**. The lower plate has a circular recess or depression **21** of the same diameter as the counterbore so that these spaces when matched form a cylindrical opening as shown. In this space in addition to the membrane **20** is a paper filter or spacer member **22** which is between the membrane and a porous plate or disc **24** which may be of suitable material such as stainless steel.

The paper filter facilitates easy transmission of demineralized water to the porous plate. The porous plate fits against spacer member **25** which is in the bottom of the depression or space **21**. The upper plate has an annular groove **27** in which is disposed a sealing O-ring **28** which seals the peripheral edges of the membrane **20**. Numeral **31** designates an opening in the upper plate for the inlet of the feed water or solution which passes through channel **32** which has a branch **33** leading to the solution reservoir **16**.

FIGURE 1.1: HIGH-FLOW POROUS MEMBRANES



(a)(b) Detail of Filtration Cell
(c) Flow Diagram, Desalinization Assembly (continued)